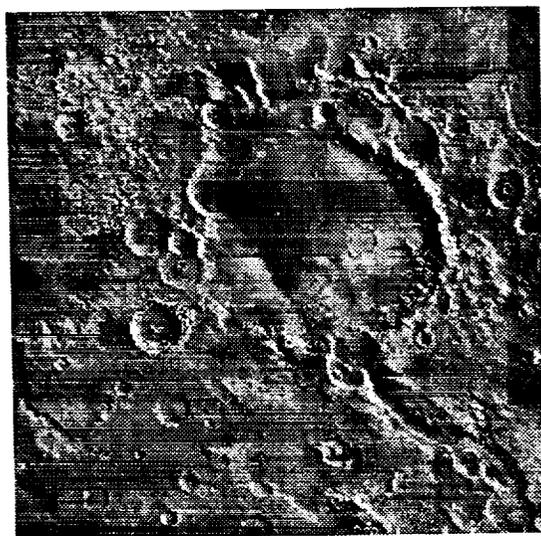
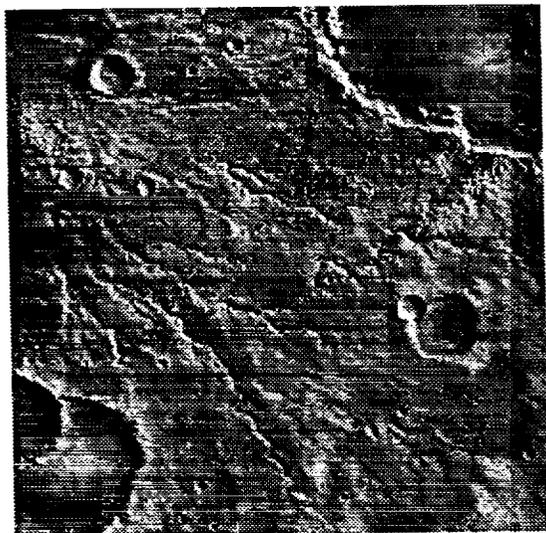


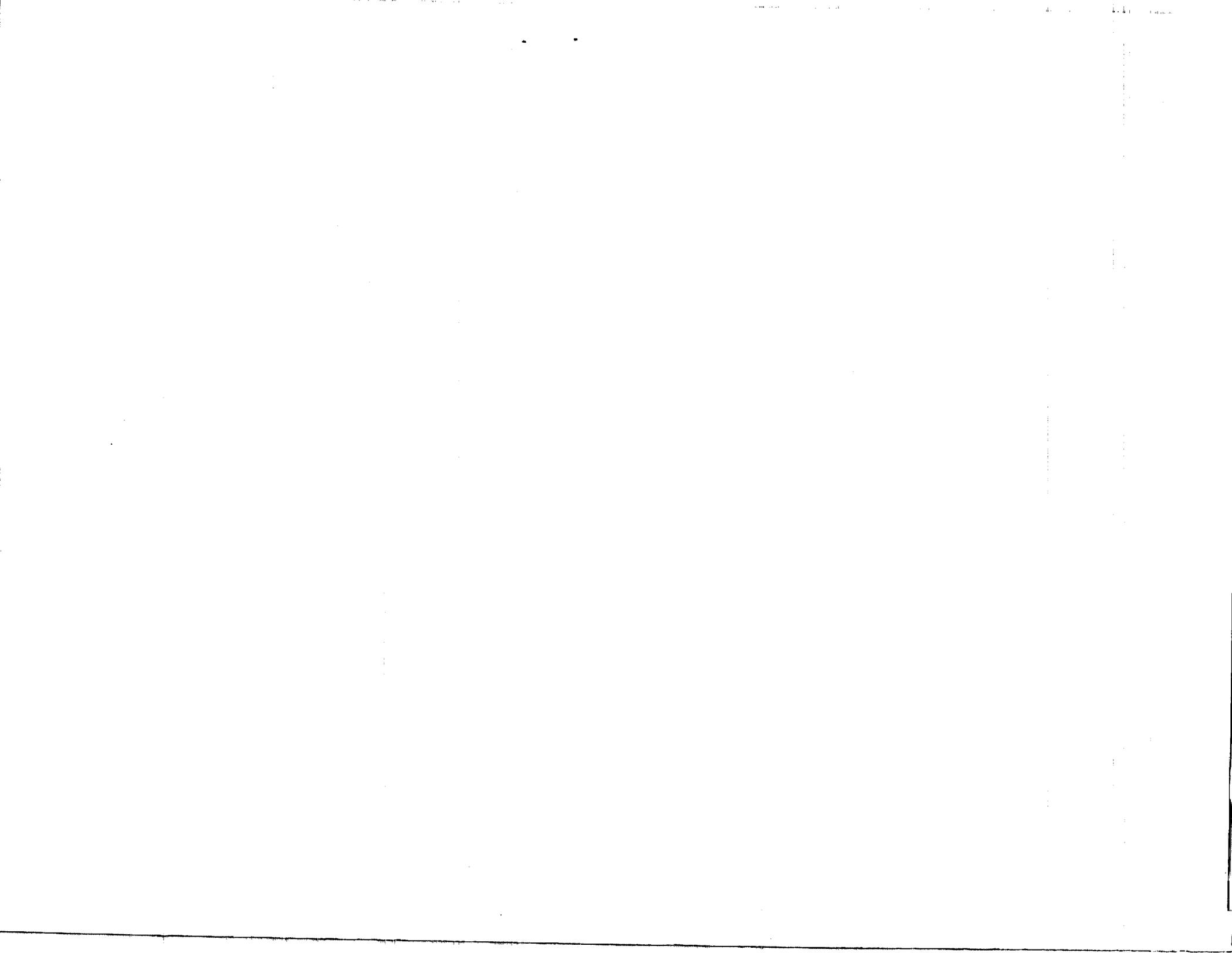
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MARS 2005 SAMPLE RETURN WORKSHOP



LPI Technical Report Number 97-01

Lunar and Planetary Institute 3600 Bay Area Boulevard Houston TX 77058-1113
LPI/TR--97-01



**MARS 2005 SAMPLE RETURN
WORKSHOP**

Edited by

V. C. Gulick

Convened by

**G. Briggs, J. Farmer, M. Carr, H. McSween, and M. Drake
at the request of J. Rahe**

**Held at
NASA Ames Research Center**

March 25-27, 1996

**Sponsored by
NASA Headquarters**

Lunar and Planetary Institute 3600 Bay Area Boulevard Houston TX 77058-1113

**LPI Technical Report Number 97-01
LPI/TR--97-01**

Compiled in 1997 by
LUNAR AND PLANETARY INSTITUTE

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Gulick V. C., ed. (1997) *Mars 2005 Sample Return Workshop*. LPI Tech. Rpt. 97-01, Lunar and Planetary Institute, Houston. 91 pp.

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Introduction

Convened at the request of Dr. Jurgen Rahe of the NASA Office of Space Science, the purpose of this workshop was to reexamine the science issues that will determine how an optimum sample return mission would be carried out in 2005 given the new context that has emerged for Mars exploration since the last such workshop was held (in 1987). The results and summary of discussion that took place at the meeting are contained in this volume. The community was invited to participate in the preparation of the final written report by browsing through the agenda and reading the text and viewgraphs provided by workshop participants and submitting comments for that section.

The workshop was organized by Dr. Geoffrey Briggs of NASA Ames Research Center with the assistance of session chairs Jack Farmer, Michael Carr, Harry McSween Jr., and Michael Drake. Assistance with workshop logistics and preparation of this report were provided by the staff of the Publications and Program Services Department of the Lunar and Planetary Institute.

Program

Monday morning, March 25, 1996

8:30–8:45 a.m. Introduction, Purpose, Approach **—Jurgen Rahe
Geoff Briggs**

REVIEW OF MARS SURVEYOR PROGRAM

8:45 a.m. Science **—Steve Squyres**

9:00 a.m. Missions Pre 2005, 2005, 2007, etc. **—Donna Shirley**

9:15 a.m. Specific Constraints for 2005 **—Jim Campbell**

10:00 a.m. Planetary Protection **—Michael Meyer**

10:15 a.m. Review of HEDS Plans for Mars **—Michael Duke**

10:30 a.m. BREAK

10:45 a.m. DISCUSSION

11:15 a.m. Phobos Sample Return Workshop:
Programmatic Context **—Alexander Zakharov**

11:45 a.m. Atmospheric Samples **—Toby Owen**

12:15 p.m. DISCUSSION

12:30 p.m. LUNCH

Monday afternoon, March 25, 1996

EXOBIOLGY Chair: Jack Farmer

1:30 p.m. Overview of the Mars Exobiology Strategy **—John Kerridge**

1:55 p.m. DISCUSSION

2:15 p.m. Exploring for a Martian Fossil Record **—Jack Farmer**

2:35 p.m. DISCUSSION

2:55 p.m. BREAK

- 3:10 p.m.** Exploring for Prebiotic Chemistry —**Jeff Bada**
- 3:30 p.m.** DISCUSSION
- 3:50 p.m.** Biogeochemical Processes —**David Des Marais**
- 4:10 p.m.** DISCUSSION
- 4:30 p.m.** Session Summary and Discussion —**Jack Farmer**
- 5:30 p.m.** ADJOURN

Tuesday morning, March 26, 1996

8:00 a.m.–12:00 noon

CLIMATE HISTORY

Chair: Michael Carr

- Current Perceptions Concerning Climate Change —**Michael Carr**
- Geologic Evidence for Climate Change —**Michael Carr**
- Chemical and Isotopic Evidence for Climate-Sensitive Processes —**Bruce Jakosky**
- Modeling Implications for Climate Change —**Bob Haberle**

SAMPLE RETURN NEEDS

- Atmosphere and Polar Deposits —**Bruce Jakosky**
- Igneous Rocks and Impact Breccias —**Laurie Leshin**
- Regolith, Sedimentary Deposits, Chemical Precipitates —**Michael Carr**

CONCLUSIONS

DISCUSSION

- 12:00 noon** LUNCH
- 12:45 p.m.** Marsokhod Demonstration in High Bay of Building 269

Tuesday afternoon, March 26, 1996

1:30–5:30 p.m.

GEOLOGY RESOURCES

Chair: Hap McSween

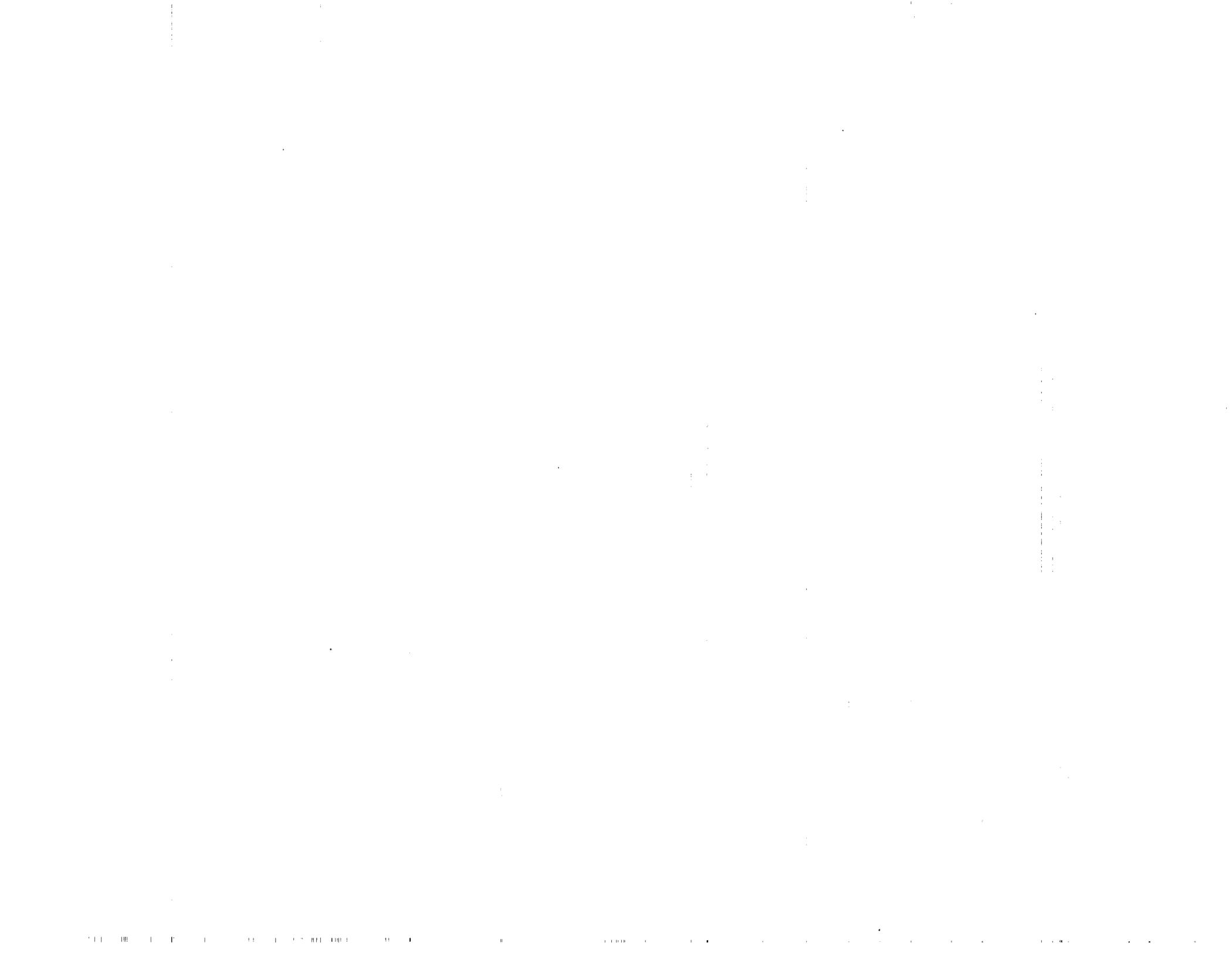
Martian Volatiles and Isotopic Signatures	—Don Bogard
Martian Interior	—John Longhi
Martian Surface Geology	—Ron Greeley
Martian Surface Materials	—Allan Treiman
Resources and Other Sampling Issues	—Hap McSween Allan Treiman

Wednesday morning, March 27, 1996

SUMMARY

Chair: Mike Drake

8:00 a.m.	Phobos Sample Return Workshop Results	—Alexander Zakharov
8:45 a.m.	Integrated Science Recommendations for 2005 MSR	—Mike Drake et al.
9:45 a.m.	DISCUSSION	
10:30 a.m.	BREAK	
10:45 a.m.	Roundtable Summary Views of All Participants	
11:15 a.m.	Summary Comments	—Steve Squyres
12:00 noon	WORKSHOP CONCLUDES	



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Dr. Jurgen Rahe
Code SL
NASA Headquarters
Washington, DC 20546

Dear Jurgen:

The Mars Science Working Group met at NASA Ames on March 27th and 28th. I was very pleased that you were able to join us for part of the meeting. I am writing to you to summarize our key findings and recommendations.

The primary purpose of this meeting was to consider the scientific issues associated with a Mars sample return mission. In order to involve a broad segment of the Mars science community in this effort, our meeting was preceded by a two and a half-day workshop, hosted by Geoff Briggs. We greatly appreciate the support that NASA provided for this activity. Geoff will be producing a detailed workshop report the coming weeks. In the paragraphs below, I will summarize what will be the major conclusion of that report.

First, we feel that the long-term focus for a program of sample returns from Mars should be to determine whether life has ever existed on Mars. This includes not just the search for life itself, but also assessment of past climatological and geological conditions on the planet, and whether they were suitable for the development of life. We believe that this focus addresses one of the most profound questions in planetary science. We also note that answering it will require careful investigation of many scientifically important characteristics of Mars.

Mars is a very complex planet, and we cannot hope to do this job with a single sample return mission. A carefully-planned campaign of sample returns will be required. We note that the resources of the Mars Surveyor program are modest, and that the first sample return mission will probably have to be very simple — perhaps little more than a technology demonstration mission — in order to be affordable. This simplicity may apply in many areas: landing accuracy, mobility, and sample selection, acquisition, handling, and preservation. A simple approach will inevitably limit the scientific value of the first samples, and it is essential that both NASA and the science community recognize this fact. Subsequent sample returns can become more complex and ambitious as we learn more about Mars and as technological capabilities improve.

A point that we discussed at length was how the missions that precede the first sample return can contribute to the scientific value of the samples. Because samples can be collected most effectively from an environment that is known and understood a priori, there are clear scientific benefits to getting the samples from a site that has already been explored on a previous mission. There may also be technical benefits to such an approach. We therefore suggest that suitability for subsequent sample return should be a factor in selection of sites for landers sent to Mars prior to the actual first sample return mission.

We also considered in more general terms how much information about Mars is needed to allow for intelligent sample return site selection. We concluded that the currently-planned set of NASA Mars missions will provide the data needed to allow selection of a scientifically adequate first sample.

The most serious gap in our knowledge of Mars that will be left by the currently-planned mission set and that is related to sample site selection has to do with surface mineralogy. After Mars Global Surveyor and Mars '96, we will have mineralogical data in the 5-50 micrometer region at 3 km/pixel, and in the 1-5 micrometer region at tens of km/pixel. Improving our ability to recognize mineralogy using visible through mid-IR data at much higher spatial resolution than this would probably allow for significantly improved sample site selection. We suggest that NASA consider augmenting the present mission set with such a capability when the opportunity to do so arises.

Some capabilities will be essential for any mission. Two of the most obvious ones are surface mobility and compositional sensing ability. Even at the simplest of landing sites, considerable geologic diversity is expected due to processes like cratering that mix materials from a range of depths. The ability to detect compositional differences among prospective samples is required to recognize diversity. In fact, for some biology-related sampling objectives, like finding carbonates, good compositional measurements may be needed to locate a useful sample at all. The ability to move around on the surface is required to take advantage of diversity, and will become increasingly important at complex and interesting sites. Because the scientific quality of returned samples will depend on the mobility and compositional sensing capability of the sample return mission vehicle(s), high priority should be placed on developing these capabilities, and on working them into the sample return campaign as soon as possible.

Accurate landing is another capability that is important for science and that should be developed soon. For the first sample return mission the target material must cover an area larger than the landing error ellipse. A small landing ellipse would therefore make a large number of prospective materials available for investigation.

Most thinking to date about a Mars sample return has focussed on rocks and soils. However, we point out that it is also scientifically important to return a sample of the martian atmosphere. The details of atmospheric composition can hold many important clues to the evolution of the planet's volatiles and climate. Fortunately, it may be technically simple for some atmospheric gas to be captured along with the surface samples. We hope that this objective can be accomplished early in the sample return campaign. There is no need to isolate the atmospheric gas from the other samples on the first sample return mission, though it would be desirable to do so on some subsequent mission so as to avoid the possible effects of rock or soil devolatilization.

There was a great deal of discussion of the types of sample sites that should be given highest scientific priority. We identified three particularly attractive types of sample site, all of which should be visited at some point in a comprehensive sample return campaign. They are, in no particular order:

- * Crustal rocks from the ancient cratered highlands
- * Sediments from an ancient lakebed
- * Volcanic plains materials of intermediate age

The workshop report will describe the scientific objectives associated with each of these in detail. We have looked at these three site types from the standpoint of the three goals of the Mars exploration program: Life, Climate, and Resources. For each of these three goals, the priorities among the site types are as follows:

Life: Ancient lakebed sediments have highest priority, with ancient highland crust second, and volcanic plains third.

Climate: Ancient highland crust and ancient lakebed sediments have high and approximately equal priority, with volcanic plains third.

Resources: All three are of high priority.

While the scientific priorities appear clear, the technical challenges associated with each type of site are not yet well known. A choice among them for the first sample return mission will have to wait until the capabilities of that mission are better understood.

A number of other issues dealing with sample masses, sample selection procedures, sample preservation, and sample curation were addressed at the workshop. These will be discussed at greater length in Geoff's report.

While our primary focus was on early sample return missions, we also gave some preliminary thought to science that could be done much later in a sample return campaign. Types of sites that would be attractive later in the campaign include:

- * Any of the three site types listed above that are not visited early in the campaign.
- * Active or recent hydrothermal sites. These could be difficult to find, but might be the most attractive candidates for supporting recent or present martian life.
- * A polar site from which a returned sample could contain a detailed record of recent climate change.
- * A site in the Valles Marineris, where there is some evidence that layered deposits were laid down in large lakes (though more recently than the ancient lakebed sites given highest priority).
- * Volcanic materials of varying ages that would allow accurate calibration of Mars' crater density-age curve.

We can also identify some technological capabilities that should be added to the program in this timeframe. These include the ability to rove over large regions (many tens of kilometers or more), the ability to sample deep in the regolith (depths of meters), and the ability to drill short distances (centimeters) into large, strong rocks and extract samples from their interiors.

While our emphasis here has been on sample return, we stress that some key Mars science objectives in the Life-Climate-Resources triad require other sorts of missions. Important examples are an array of seismometers to investigate internal structure (this will be done to some extent by InterMarsnet), a large array of meteorological stations to investigate atmospheric circulation, and an aeronomy orbiter to investigate the upper martian atmosphere and its interaction with the solar wind.

In addition to sample return, we also dealt with two topics related to international cooperation at Mars: InterMarsnet and Mars Together.

Heinrich Wänke brought us up to date on the status of the InterMarsnet selection, and Jeff Plescia explained to us NASA's position: that NASA will support InterMarsnet if and only if it is selected by ESA this spring for a 2003 launch. We support this position. We also reaffirm the strong scientific endorsement that we gave InterMarsnet at our last meeting. Moreover, we note that InterMarsnet could be a very effective scientific precursor to a sample return mission by characterizing three prospective sample sites in detail. The three model landing sites discussed in the InterMarsnet Phase A Report are from intermediate-age volcanic plains, ancient cratered highlands, and an ancient lakebed. These are the same three types of sites we have endorsed for sample return, and we feel that InterMarsnet could go a long way toward performing scientific validation of such sites.

Roger Bourke, Pete Ulrich, and Sasha Zakharov spoke to us about Mars Together. We were impressed by both the scientific return and the risk of this venture. There was a good deal of discussion of the "launch vehicle dividend" that this mission might provide. This dividend was defined to us as the amount of money that NASA will save by using a Russian launch vehicle in 2001, minus the amount NASA will spend as a consequence of doing business with Russia. The magnitude of this dividend is not known now, nor even whether it is positive or negative. We were pleased to hear from Roger that a very high priority will be placed on estimating soon what this dividend might be. We also note that there are other potential benefits like increased launch mass. Until we know what the financial and technical benefits of Mars Together are, we must restrict our comments on Mars Together to purely scientific issues.

We note that Mars Together, if successful, can provide an enormous scientific dividend. Along with delivering one of NASA's planned 2001 missions to Mars, it would also allow a substantial Russian landed element (nominally a rover) to be placed on the surface. Because of the science that this Russian vehicle might generate, we endorse Mars Together even if the financial dividend proves to be zero. We assume, of course, that data from all Mars Together spacecraft would be shared by both the US and Russia.

We are concerned with the apparent risks associated with Mars Together. These risks seem to be more programmatic than technical, and at the moment they are difficult to assess. At a minimum, we feel that it would be unwise to let participation in Mars Together jeopardize the science on the US-launched 2001 mission. This could happen, for example, if the launch vehicle dividend were negative and large. Imprudent risk, both technical and programmatic, to the Russian-launched mission must also be avoided, and we are prepared to provide advice on the science trades in this area as the risks become better understood.

Our hope, of course, is that the financial dividend will be positive. If it is, we can think of a number of ways it could be used to enhance the overall science of Mars Together. These include the following:

- * Paying for some modest US instrumentation on the Russian landed element.
- * Paying for integration of some modest Russian instrumentation on one or both of the US spacecraft.
- * Improving the landing accuracy of the US 2001 lander.
- * Helping to provide a rover for the US 2001 lander.
- * Paying for more science instrumentation on the US 2001 lander or orbiter.

The scientific benefits of these uses are quite variable, and we are prepared to prioritize among them on scientific grounds once an estimate of the size of the financial dividend is available.

That summarizes the major findings and recommendations from our meeting. As always, please contact me with any questions or comments that you might have. Our next meeting will be in Washington, DC on August 1st and 2nd. I hope that you'll be able to join us for that one as well.

Best wishes,

Steve Squyres
Chairman, MarsSWG

cc: W. Huntress
P. Ulrich
H. Brinton
J. Plescia
J. Boyce
C. Pilcher
G. Cunningham
A. Spear
J. McNamee
N. Haynes
D. Shirley
R. Bourke
S. Miller
J. Campbell
L. Lowry
C. Weisbin
A. Chicarro
G. Scoon
A. Zakharov
Mars SWG members



Workshop Presentations

Review of Mars Surveyor Program

Steve Squyres, Cornell University—

Mars Surveyor Science

Mars Surveyor Science 1996

Mars Global Surveyor

- ❖ High-resolution surface morphology
- ❖ Synoptic global imaging
- ❖ Mineralogy (~5–50 mm)
- ❖ Topography
- ❖ Gravity field
- ❖ Occultation profiles
- ❖ Magnetic field

Mars Pathfinder

- ❖ Surface morphology
- ❖ Mineralogy (~0.4–1.0 mm)
- ❖ Meteorology
- ❖ Elemental chemistry
- ❖ Entry profile

Mars Surveyor Science 1998

Orbiter

- ❖ Atmospheric sounding: P/T structure, water, dust
- ❖ Multispectral imaging

Lander

- ❖ Polar layered deposits
- ❖ Morphology
- ❖ Stratigraphy
- ❖ Mineralogy/ice content
- ❖ Meteorology
- ❖ Entry profile

Mars Surveyor Science 2001

Orbiter

- ❖ Global elemental chemistry
- ❖ Subsurface H₂O (to <100 cm)
- ❖ Something else? Imaging? NIR spectrometer

Lander

- ❖ Mars SWG recommends landing in ancient highlands with focus on ancient climate and water
- ❖ Payload is TBD

Mars Surveyor Science '03

Either InterMarsnet

- ❖ 3 NASA landers, ESA orbiter
- ❖ Seismic network: Seismicity and internal structure
- ❖ Atmospheric science: Surface meteorology stations and a supporting orbital sounder
- ❖ Morphology, mineralogy, and geochemistry at three sites

Or something else???

Where will we be in 2005?

We'll have a good global view of the planet's surface and atmosphere: morphology, mineralogy, geochemistry, topography, gravity, magnetics, atmospheric, transport

We'll have a detailed look at morphology, mineralogy, geochemistry, and meteorology at six surface sites (plus Viking sites, plus Russian landing sites)

We'll know something about the planet's internal structure

Michael A. Meyer, NASA Headquarters—

Planetary Protection and Mars Sample Return

Committee on Space Research

The U.S. is signatory to a 1967 international treaty, monitored by COSPAR, that establishes the requirement to avoid forward and back contamination of planetary bodies during exploration.

Planetary Protection

Purpose

Preserve biological and organic conditions for future exploration

Protect the Earth and its biosphere

Scope and Applicability

All missions to planetary bodies, and all missions that return to Earth from a target exploration

Policy

Some mission will require controls on forward contamination

Earth must be protected from the potential hazard of returned extraterrestrial samples

Mission Constraints

Depends on the nature of the mission, on the target planet, and current knowledge, based on internal and external recommendations, most notably from the Space Studies Board

1992 SSB Report

Key Findings

Probability of growth of terrestrial organisms on present-day Mars is essentially zero

Bioload reduction for all missions to the surface is still minimize chances of jeopardizing future experiments

Recommendations

“Landers carrying instrumentation for in situ investigation of extant martian life should be subject to at least Viking-level sterilization procedures”

Spacecraft (including orbiters) without biological experiments should be subject to at least Viking-level presterilization procedures - such as clean-room assembly and cleaning of all components—for reduction of bioload, but such spacecraft need not be sterilized”

1992 SSB Report

Sterilization of outbound spacecraft

Hermetically sealed Mars sample container

Break the chain of contact with Mars

Quarantine and testing

Planetary Protection Classification of Missions
Planetary Protection Mission Categories

Planet	Priorities	Mission Type	Mission Category
A	Not of direct interest for understanding the process of chemical evolution. No protection of such planets is warranted and no requirements are imposed.	Any	I
B	Of significant interest relative to the process of chemical evolution but only a remote chance that contamination by spacecraft could jeopardize future exploration.	Any	II
C	Of significant interest relative to the process of chemical evolution and/or the origin of the order, which scientific opinion provides a significant chance of contamination that could jeopardize a future biological experiment.	Flyby, Orbiter	III
		Lander, Probe	IV
All	Any solar system body.	Earth-Return	V

Space Studies Board Issues

The potential for a living entity to be returned in a sample from another solar body, in particular Mars.

Scientific investigations that should be conducted to reduce the uncertainty in the above assessment.

The potential for large-scale effects on Earth resulting from release of any returned entity.

The status of technological measures to prevent inadvertent release.

Criteria for intentional release.

Planetary Protection

Developing an environmental impact statement

 Develop timeline and determine what information is needed

Sealing and preserving the Mars sample

 To ensure no accidental release

 To ensure no terrestrial biological contamination

Breaking the contact chain with the surface

 Review previous and novel approaches

 Identify technological readiness

Quarantine testing of the returned sample

 Suitability of P4 facilities for MSR

 Review Apollo and new methods for biohazard testing

Science Return for PP

Allay public fears of a returned sample

Reduce future constraints on sample return missions

Reduce or eliminate biohazard testing before sample release

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Michael B. Duke, Lunar and Planetary Institute—

Human Exploration and Development of Space and the Mars Sample Return Mission

The Human Exploration and Development of Space is one of NASA's five strategic enterprises, which comprise the major thrusts of the U.S. space program. This enterprise includes all NASA programs that involve human space flight, including the space shuttle, International Space Station, and future exploration programs beyond low Earth orbit. The management of HEDS is currently shared by the Office of Space Flight and the Office of Life and Microgravity Science and Applications, but also incorporates significant contributions from the Office of Space Science and the Office of Access and Space Technology. In other words, essentially all parts of NASA are involved in the Human Exploration and Development of Space.

As a new strategic enterprise, HEDS has completed its first Strategic Plan. This can be downloaded from the Internet at <http://www.osf.hq.nasa.gov/heds/hedsplan.html>. For the first time, NASA enunciates, in HEDS, the goal to "Explore and Settle the Solar System." Within this strategy are two specific objectives of importance to Mars exploration. The first is: "Characterize solar system bodies, including the Moon, Mars and asteroids, to enable planning for human activities." Another calls for "Demonstrate technologies required to use extra terrestrial resources." Another major objective calls for NASA to "Establish a human presence on the Moon, in the Martian system, and elsewhere in the inner solar system." The strategies within this emphasize the development and demonstration of technologies to support humans and to undertake human exploration missions at drastically lowered cost. This strategic approach provides the basis for consideration of the linkages between robotic missions and the initial human exploration of Mars.

In 1993-1994, a review and development of a human exploration of Mars reference mission was undertaken by an intercenter group. This report is nearing publication and should be available soon as a NASA SP. The reference mission established a number of desirable features of a human Mars exploration program, including long-duration surface operation and extended surface exploration mobility, supported by a robust surface infrastructure that utilizes *in*

situ resources for life support and propulsion. A buildup of infrastructure over four Mars launch opportunities was envisioned, which allowed local to regional exploration for science, and addressed of the critical questions regarding the feasibility of permanent habitation of Mars. The contributors to the reference mission report believed that the program outlined could be undertaken (three human landings, each lasting 1.5 years on the martian surface) for about the cost of the Apollo program adjusted for inflation.

One purpose of this reference mission was to provide a basis for understanding the importance of various technology developments and improvements that could be undertaken between now and the time a human exploration program can be initiated. This serves as well as a means of identifying technology demonstrations and information gathering that can be done by robotic missions in advance of the human missions. In particular, a Mars Sample Return Mission can contribute particularly to (1) gathering environmental and sample data, which includes dust composition and size distribution, surface dust and surface environment reactivity, as well as generally gathering ground truth through which the large bank of Mars remote sensing data can be calibrated; (2) demonstrating and verifying the extraction of useful resources from the martian atmosphere, the high power applications required to do that, and the system control that will be necessary for long-lived operations; (3) test and verify sample collection and packaging using teleoperated rovers, preserving and packaging samples and back-contamination control; and (4) demonstrating an end-to-end round-trip mission to Mars that could include aerocapture, precision landing surface operations, including remote checkout of the Mars Ascent Vehicle from Earth, fueling with ISRU, Mars launch, Mars orbital rendezvous/dock, and return trajectory management.

The Human Exploration and Development of Space is linked inevitably to the robotic missions such as the Mars Sample Return Mission, which provides both fundamental data as well as a demonstration testbed for important technologies.

Viewgraphs presented at meeting—

HEDS Exploration Planning

Strategic plan

Implementation strategies

Technology

Advanced development

Reference Mission

Long-duration surface operation

Nuclear surface power

Closed life support system

Extended surface exploration

In situ resource utilization for life support and propulsion

Consumables caches

Split-mission strategy

Fast-transit crew transfers

High-performance cargo transfers

Rendezvous on surface

Three human landings at outpost site

Very-long-lived systems (10 years)

Short human trip times (4 months)

Nuclear thermal TMI stage

HEDS Development Needs

Transportation systems

Earth to orbit

In-space

Transportation technologies

Aerobraking

Orbital rendezvous/docking

Autonomous landing

Cryogenic fluid management

Surface systems/technologies

Personnel EVA systems

Regenerative life support

Surface nuclear power

Teleoperated mobility systems

Human-operated mobility systems

In situ resource extraction

Long-lived systems

HEDS Development Needs

Human support

Radiation protection

Health care

Human factors

Science systems

Sample acquisition and analysis

Operations systems

Autonomous electronic and mechanical device operation, maintenance, and repair

Information

Environmental degradation of materials

Resource availability

Science site selection data

Landing site safety characterization

Trafficability

Contributions of Robotic Missions

The development and/or demonstration of these capabilities on robotic missions will directly influence human mission design, development, and operations.

	Decrease Cost	Decrease Risk	Increase Performance
Aerobraking	X		X
Orbital rendezvous	X	X	
Advanced propulsion	X	X	X
<i>In situ</i> resource utilization	X	X	X
Pinpoint, autonomous landing	X	X	
High-performance electric power	X	X	X
Cryogenic fluid management	X	X	
Surface mobility	X	X	X
Autonomous, long-lived systems	X	X	
End-to-end operations tests		X	
Effective management systems	X	X	
Science site selection			X
Radiation environment		X	
Surface materials hazards (e.g., dust)		X	
Refine back-contamination issues	X	X	
Site safety characterization		X	
Resource availability	X	X	
Trafficability		X	X
Improve training simulations		X	X
Emplace beacons, presample site		X	X

Mars Sample Return Relationship to Human Mars Reference Mission

Environmental and sample data

Dust composition and size distribution

Surface environment reactivity

Geological ground truth

Resource extraction demonstration

Extraction process

High power demonstration

System autonomy and control

Sample collection and packaging

Teleoperated rover sample collection

Preservation and packaging

Back-contamination issues

End-to-end round-trip Mars mission demonstration

Aerobraking

Precision landing; landing site alterations

Surface operations, including remote checkout of MAV from Earth

Fueling with ISRU

Mars launch

Rendezvous/dock

Return trajectory management

Tobias Owen, University of Hawai'i—

Atmospheric Samples

It will be impossible to reconstruct the origin and early history of the martian atmosphere without a detailed knowledge of the present composition, including isotope ratios of the various elements. This knowledge must be extended to gases trapped in rocks, adsorbed on soils and condensed as ices. Only in this way can we determine the importance of various escape processes and identify current volatile reservoirs.

The study of the martian atmosphere has greater significance than simply learning more about the atmosphere itself. We need to know the early history of the atmosphere in order to understand the early history of water on the planet and the associated probabilities for the origin and early evolution of life. The discovery of a trace constituent such as methane, which is far from chemical equilibrium in the present martian atmosphere, would be a clue that life might actually exist on Mars today. Because Mars is relatively inactive geologically, it preserves a record of the first billion years that is almost completely missing on Earth. We can therefore hope to use the study of the martian atmosphere to help us understand the early history of all inner planet atmospheres.

As an example of how that can be done, I can offer an outline of a model Akiva Bar-Nun and I have developed for bringing in

volatiles with icy planetesimals [1]. This is illustrated in the accompanying viewgraphs. One aspect of our argument that is worth noting here is the importance of many martian samples. We use noble gases from the SNC meteorites to support the idea that inner planet atmospheres may be a mixture of volatiles brought in by rocks and those contributed by icy planetesimals. If we had only the Chassigny meteorite, we would never have seen this connection.

We can certainly make further progress in understanding the martian atmosphere by means of remote investigations from Earth and by additional measurements of SNC meteorites. However, these investigations cannot substitute for direct analyses of a sample of martian atmosphere that has been brought to Earth in an undisturbed state, accompanied by suitable samples of soils, rocks, and ices. We can only achieve the necessary accuracies for stable isotope abundance determinations in suitably equipped terrestrial laboratories. These atmospheric samples should therefore be an essential component of any sample return program.

References: [1] Owen T. and Bar-Nun A. (1995) *Icarus*, 116, 215-226.

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Viewgraphs presented at meeting—

Atmospheric Sample Return

History of climate

History of volatiles

Origin and early evolution

- ❖ Of atmosphere?
- ❖ Of water?
- ❖ Of life?

Require excellent knowledge of today's atmosphere

Composition

Isotope ratios

Opportunity to study origin of ALL inner planet atmospheres

Mars

Present atmosphere

Low abundances of noble gases per gram of planet

High values of

- ❖ $^{129}\text{Xe}/^{132}\text{Xe} = 2.5 \times \text{Earth}$
- ❖ $^{40}\text{Ar}/^{36}\text{Ar} = 10 \times \text{Earth}$
- ❖ $^{15}\text{N}/^{14}\text{N} = 1.6 \times \text{Earth}$
- ❖ $\text{D}/\text{H} = 6 \pm 2 \times \text{Earth}$

Very low carbon and nitrogen in atmosphere

- ❖ $P_s \sim 7 \text{ mbar}$

Chondritic noble gas pattern

- ❖ Do not fit:
 - ◆ Mars
 - ◆ Earth
 - ◆ Venus

Hypothesis

The origin and evolution of inner planet atmospheres were dominated by impacts
Brought volatiles in — “ingassing”

Blew volatiles away — impact erosion

The dominant source of volatiles was a spectrum of icy planetesimals

Did They Really Do It?

Clues:

Heavy noble gases

- ❖ Don't escape
- ❖ Don't react chemically

Argon, krypton, xenon

Assume

Atmospheres have two sources of Ar, Kr, Xe:

Internal—rocks

External—comets

Mars and Earth have "same" (i.e., same two sources; different proportion)

Rocks

Bombardment

Atmospheres then consist of mixtures of these two volatile reservoirs

Comets as the External Source

Problem: No data!

Solution: Laboratory simulations

—Akwa Bar-Nun et. al., Tel-Aviv University

Deposit ice at low temperatures (15–150 K) in presence of mixtures of gases

Proportions of noble gases trapped in ice depend on temperature

Results: (from Bar-Nun Experiments)

T ~ 30 K

Kuiper Belt comets

- ❖ All three gases trapped equally
- ❖ Retain solar mixture

T ~ 50 K

Uranus-Neptune comets (Oort cloud)

- ❖ Argon depleted (fractionation)
- ❖ Resembles Mars-Earth atmosphere mixture

Things to Consider (1):

Escape

Early

- ❖ Hydrodynamic
- ❖ Impact erosion

Continuing

- ❖ Jeans
- ❖ Sputtering
- ❖ Predissociative

Reservoirs

Ice

Regolith

Photochemistry

Nucleogenesis

Things to Consider (2):

V. Krasnopolsky—

Oxygen and carbon isotope ratios depend on
Present water amount

Present regolith-cap reservoir of CO₂

Present carbonate abundance

Total escape of H₂O

Total escape of CO₂

Initial abundance of CO₂

The Importance of CHANCE

Atmospheres are tiny fractions of planetary masses

Random hits make a big difference!

PLUS!—MINUS!

Exobiology

John F. Kerridge, University of California at San Diego—

An Exobiological Strategy for Mars Exploration

In 1994, a writing group was convened by Dr. Michael A. Meyer, Discipline Scientist for Exobiology at NASA HQ, and charged with the task of formulating a strategy for the exobiological exploration of Mars. This group (1) reviewed the state of knowledge about Mars as a planetary environment, (2) defined the major exobiological goals that could be addressed by exploration of Mars, (3) showed how achievement of those goals would require a sequence of robotic missions culminating in return of a martian sample to Earth, (4) summarised the status of planned missions to Mars in this country and elsewhere, (5) discussed the key role of site selection in achieving exobiological goals, and (6) made a series of recommendations, including several regarding development of technology for future missions. Because of the key role envisaged for sample return in exobiological exploration, and the fundamental scientific importance of resolving the question of whether life ever arose on Mars, it seemed appropriate to include a summary of the group's findings [1] in the report of the Mars Sample Return Science Workshop.

Prior to the Viking missions, exobiological interest in Mars centered on answering the question: Is there life on Mars? However, the emphasis shifted significantly as a result of those missions: Viking revealed a martian surface that today appears highly inhospitable to life, but also dramatically confirmed earlier suggestions that in the past the surface of Mars was heavily affected by liquid water, implying significantly warmer and wetter conditions than pertain today. Furthermore, in the years since Viking, much has been learned about the nature and timing of the earliest life on Earth, and also about the environmental limits within which life can exist on Earth today. The confluence of these findings leads to the following conclusion: Early environments were apparently sufficiently similar on Mars and Earth, and life arose so rapidly on Earth once conditions became clement, that emergence of life on both planets is scarcely less plausible than emergence on only one.

The major exobiological goals for Mars exploration may be defined as:

- ❖ To what extent did prebiotic chemical evolution proceed on Mars?
- ❖ If chemical evolution occurred, did it lead to synthesis or replicating molecules, i.e., life, that subsequently became extinct?
- ❖ If replicating systems arose on Mars, do they persist anywhere on Mars today?

Although the writing group devised strategies for addressing all three goals, they noted that the Viking results make it likely that any contemporary life on Mars must be well shielded from the hostile surface environment and consequently hard to detect by spacecraft. However, evidence of past life, though potentially vulnerable to destruction at the very surface, could be preserved in relatively accessible locations, such as the interiors of impermeable sedimentary rocks deposited during the epoch of intense aqueous

activity on Mars. (The survival of such rocks on Mars is greatly enhanced relative to the Earth because of the subsequently dry climate, low temperatures, and lack of tectonic overprinting on the former.) Furthermore, conditions suitable for preservation of evidence for extinct life would also be ideal for preservation of a record of prebiotic chemistry, in the event that life failed to arise. Consequently, a properly planned search for evidence of extinct life on Mars would have a high probability of yielding evidence for possible prebiotic chemical evolution, even if its primary goal were not achieved. For the foreseeable future, therefore, the emphasis of the exobiological exploration of Mars will be on the search for evidence of an ancient biosphere.

It quickly became apparent that the search for evidence of past life on Mars would require a different strategy from that of Viking. Instead of one or two complex spacecraft searching directly for evidence of extant metabolic activity, it would be necessary to mount a campaign, consisting of a series of relatively small missions, each building upon the results of its predecessors, that would focus ever more closely on those samples that might have preserved evidence for ancient life or ancient organic chemistry. The initial task would be site selection. This would involve orbital missions capable of identifying promising lithologies on the martian surface by means of their IR spectra and determining their global distribution. Typical target lithologies would be aqueously deposited chemical sediments, such as cherts, carbonates, or phosphates, which are known to be effective at preserving biosignatures on Earth. (The term "biosignature" refers to any piece of evidence indicative of the former presence of life. Examples could include biofabrics, microfossils, chemical biomarkers, or isotopic signatures characteristic of bioprocesses.) Because the spatial scale of such deposits on Mars is presently unknown, and because of the difficulty of resolving mineral mixtures using such spectral data, the acquisition of IR data at high spatial resolution (30–100 m/pixel) from selected locations is considered necessary.

Although the group considered the feasibility of *in situ* robotic detection of evidence for extinct life, it concluded that acquisition of such evidence on a returned sample would be necessary. The reasons are twofold: first, the vastly greater scope of analytical procedures available in a terrestrial laboratory; and second, the likelihood that the science community would require that such an epochal finding, if made robotically, be confirmed in the laboratory. Consequently, the search for ancient life on Mars would culminate logically with at least one mission dedicated to the return to Earth of a sample selected on the basis of its potential for having preserved a biosignature. Clearly, the analytical protocol employed on returned samples will require particularly tight control in order to minimize the danger of either false positives or false negatives.

Between the orbital missions and sample return, however, it will be necessary to have landed precursor missions capable of

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confirming site selection(s) made from orbit, and of selecting at the optimum site those samples that should be subsequently returned to Earth. Requirements for such precursor missions would include mobility sufficient to permit exploration and sample acquisition anywhere within the spacecraft's landing ellipse, a capability for remote surveying of individual rocks and possible outcrops with the objective of identifying promising lithologies for biosignature preservation, and a capability for confirming such remote identifications by means of chemical and mineralogical analyses in contact with selected rocks and/or outcrops. In addition, a capability to extract a sample from a few millimeters depth within a rock will almost certainly be necessary, either to avoid weathering rind or to acquire a sample of suitable size for return to Earth or both. It may also be desirable to analyze the interiors of promising rocks *in situ* for a limited range of organic compounds that might indicate either a prebiotic chemical record or the possible presence of more definitive biosignatures.

Consideration of the issues described above leads to a series of exploratory steps, each of which needs to be taken in turn if a rigorous search for ancient life on Mars is to be conducted. The writing group did not explicitly consider the timeframe on which such a sequence of missions should be carried out. However, it is fair to conclude that an optimum timeframe for such an endeavor would

place the sample return mission somewhat later than 2005. Whether launching a sample return mission in 2005 is compatible with the sequence of steps necessary to pursue one of the major exobiological goals on Mars is unclear at this time. However, it seems unlikely that such an accelerated schedule could be carried out within the constraints of the Surveyor program.

It should be noted that there are goals of secondary exobiological interest that could be pursued by a sequence of missions that conform to less stringent criteria than those given above. Such goals might include acquisition of information on volatile inventories on Mars, the timing of aqueous activity on Mars, the nature of climate evolution on Mars, etc. However, it must be pointed out that missions designed to acquire such information are unlikely to yield a reliable answer to the question: Did life ever emerge on Mars? The converse is not necessarily true, however. A properly designed campaign to bring back an optimal sample in which to search for evidence of ancient life would also provide optimal samples with which the secondary goals given above could be addressed. If suitable care is taken during the planning process, there could be a high level of compatibility among the needs of the different components of the "Goldin-Huntress" contract.

References: [1] *An Exobiological Strategy for Mars Exploration* (1995) NASA SP-530, Washington DC.

Viewgraphs presented at meeting—

Emergence of Life on Mars is Not Far-Fetched

“Early environments were apparently sufficiently similar on Earth and Mars, and life arose so rapidly on Earth once conditions became clement, that emergence of life on both planets at that time is scarcely less plausible than emergence on only one.”

—From: *An Exobiological Strategy for Mars Exploration NASA SP-530 (April 1995)*

Science Goals

To what extent did prebiotic chemical evolution proceed on Mars?

If chemical evolution occurred, did it lead to formation of replicating molecules?

If a replicating system arose on Mars, has it resulted in life anywhere on Mars today?

The Exobiological Exploration of Mars

Lessons from Viking

The surface of Mars is hostile not only to life but even apparently to abiotic organic matter

Any possible oases containing extant organisms must be well protected from the hostile surface environment and would therefore be difficult to detect by means of spacecraft

Many signatures of extinct life would also be destroyed in the present-day martian surface environment

Consequently, on Mars any possible biosignatures are likely to be best preserved in the interiors of fine-grained sedimentary rocks, as indeed they are on Earth

The goal of martian exobiology is therefore to identify such sedimentary rocks and return them to Earth

Principal Recommendations

Currently approved missions and instruments, plus

Map distribution of water

Orbital identification of aqueously altered lithologies (e.g., hydrothermal deposits, evaporites, springs)

❖ Improve spatial resolution of orbital near-IR spectrometry

Development of landed mineral-identification capability

❖ Miniaturized IR spectrometry, plus

❖ X-ray diffraction/fluorescence

Development of surface mobility with a range of kilometers

Near-term deployment of subsurface sampling devices (~1 cm depth in rock; >1 m depth in regolith)

Development of organic-analytical capability

❖ Elemental

❖ Molecular

❖ Isotopic

Continued support of basic R & A

- ❖ Biogeochemistry of relevant environments
- ❖ Mars-analog studies
- ❖ SNC meteorite analyses
- ❖ Refinement of science objectives

The Search for Ancient Life on Mars

A campaign, not a single mission

A sequence of missions, each building upon its precursors

Each step focuses ever more closely on biosignature-host rock

Even if life never emerged on Mars, the same sampling criteria could yield evidence concerning prebiotic chemical evolution

Sample return ultimately necessary

That returned sample will also be optimal for many other studies

Precursor missions to sample return driven by:

Site selection

Sample selection

Requirements for Site and Sample Selection

Site selection

Development of orbital near-to-mid IR spectral-imaging capability with high spatial resolution

Sample selection

Improvement in precision of landing ellipse

Further development of enabling rover technology

Development of robotic capability to sample rock interiors

Further development of techniques for *in situ* analysis of

- ❖ Chemical composition
- ❖ Mineralogy
- ❖ Selected organic compounds

The Search for Ancient Life on Mars

The necessary steps

Global mapping of aqueously deposited lithologies

Identification and location of biologically promising deposits

Identification of fine-grained sedimentary rocks at promising sites

Search interiors of suitable rocks for biologically relevant organic matter

Return suitable rock samples for analysis on Earth

Return of an Exobiology Sample in 2005?

The extent to which a sample return mission in 2005 will be able to address the major exobiological goals (i.e., search for evidence of ancient life or of prebiotic chemical evolution) is a strong function of the progress that can be made between now and 2005 in (1) selection of landing sites and (2) identification of the appropriate samples to be returned.

Such progress will require (1) immediate substantial investment in development of appropriate technologies (i.e., IR spectral imagery, rovers, rock "coring," XRF/XRD, organic analysis), and (2) involvement of exobiologists in planning and data analysis of precursor orbital and lander/rover missions.

Ancient Life on Mars Steps Toward an Exobiological Sample Return in 2005

1996	1998	2001	2003	2005
Site Selection-1 MGS/TES maps global sedimentary distribution of aqueously known deposited lithologies		Site Selection-2 Orbital high-resolution IR spectral imager locates suitable deposits	Sample Selection Rovers analyze interiors of rocks at selected sites for mineralogy, organics	Sample Return Return of rock sample(s) to contain organics
SUPPORTING SCIENCE				
Mars-96/MOX clarifies nature of surface oxidant(s)	Planet-B/NMS studies volatile-loss mechanisms	GRS maps global hydrogen distribution		
MGS/MOC provides high-resolution imagery of surface	MVACS investigates distribution, cycling of volatiles			
MGS/LA generates detailed topography				

General Comments

A returned sample satisfying the needs of exobiology would also be optimal for many other types of study, particularly those involving evolution of volatiles, low-temperature geochemistry, or climate change.

In order to maintain a schedule that will permit return of an exobiologically relevant sample in 2005, it will be necessary to plan each mission in light of results from the immediately preceding opportunity. This will significantly add to mission development costs.

By 2003, it will be necessary for the range of a scientifically capable rover to have become comparable to the semimajor axis of the then-achievable landing ellipse.

Probability of success would be enhanced by using lander/rovers at several different sites in 2003.

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Jack D. Farmer, NASA Ames Research Center—**Optimization of 2005 Sample Return for Mars Exopaleontology**

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Introduction: Since Viking, Mars exobiology has shifted focus to include the search for evidence of an ancient biosphere. The failure of the Viking biology experiments to detect life at the two sites sampled has been broadly accepted as evidence that life is probably absent in surface environments, a view consistent with the lack of liquid water, the high UV flux, and oxidizing conditions observed in the surface soils sampled. The detailed hydrological history of Mars is unknown. But in broad outline, it appears that clement conditions for life probably existed at the surface of Mars early in its history, particularly during the time that widespread valley networks were formed within the ancient cratered highland terranes of the southern hemisphere [1]. Crater ages suggest that this period of surface water occurred toward the end of late bombardment, perhaps 3.5–4.0 Ga, during the time that life was emerging on the Earth [2].

Despite the fact that present surface conditions are inhospitable to life, it is quite plausible that life may yet persist in subsurface environments on Mars where liquid water could be present owing to higher temperatures and pressures [3]. However, such environments are unlikely to be explored prior to manned missions, perhaps decades hence. Thus, if life ever arose on Mars, we will likely discover evidence of its former presence in the rock record at the surface long before we are able to drill for liquid water perhaps hundreds to thousands of meters beneath the surface. Clearly, the exploration for a fossil record of life on Mars requires a much different strategy than the search for extant life [4], and this strategy is presently embodied in Mars exopaleontology, a new subdiscipline of geology that borrows its scientific heritage from Precambrian paleontology, microbial ecology, biosedimentology, biogeochemistry, and Mars surface science [5].

The strategy for Mars exopaleontology is founded on a few basic principles gleaned from studies of the Precambrian fossil record, as well as studies of fossilization processes in modern environments on Earth that are regarded to be good analogs for the early Earth and Mars. Such studies reveal not only the ways in which biological information is captured and preserved in sediments, but also suggest optimal methods for extracting biological information from ancient rocks on Earth or returned from Mars.

It is noteworthy that even if life never developed on Mars, the prebiotic organic chemical record preserved there is an equally important scientific objective for exopaleontology. The absence of a plate tectonic cycle on Mars suggests that old geologic terranes may be much better represented there. The destructive processes of burial metamorphism are likely to be much less a problem on Mars, although impact metamorphism and brecciation of the surface have undoubtedly overprinted the early record to some extent. But, the prebiotic chemical record found on Mars, of vital importance in understanding the origin of life on Earth, is likely to be much better preserved, and may provide access to a record of prebiotic processes long ago destroyed on our own planet.

On Earth, >98% of all the organic carbon fixed by organisms is destroyed and recycled. The small amount of organic carbon that escapes recycling persists in the crust because it is rapidly buried in fine-grained, low-permeability sediments, and isolated from de-

structive biochemical processes. This organic carbon reservoir makes up the chemical portion of the fossil record, preserving biological information as a variety of organic biomarker compounds (e.g., hopanes, the degradation products of cell wall lipids) and isotopic signatures (e.g., characteristic carbon isotope ratios reflecting biological fractionation processes).

The preservation of organic carbon occurs under a very restricted set of geologic environments and conditions that are fairly well understood on Earth. But even where organic compounds are destroyed by oxidation, biosignatures may yet persist in sedimentary rocks as fabrics produced by microorganisms (e.g., mesoscopic features like stromatolites or related biolaminated sediments, and characteristic microfibrils contained therein) or "biominerals" (e.g., carbonates or phosphates formed as the byproduct of various physiological processes).

A basic tenet that has emerged from paleontological studies is that the long-term preservation of biological information as fossils is favored in environments where aqueous minerals precipitate rapidly from aqueous solutions, or where fine-grained, clay-rich detrital sediments accumulate very rapidly, entombing living organisms or their byproducts, before they can be degraded [6]. The most favorable aqueous minerals are those that form fine-grained, impermeable host rocks that form a closed chemical system, isolating organic materials from oxidation. Favorable host minerals are also those that are chemically and physically stable and resistant to major fabric reorganization during diagenesis.

The most favorable host minerals for the long-term preservation of organic materials are those with long crustal residence times. These tend to be minerals that are most resistant to chemical weathering. High-priority minerals in this category include silica, phosphates, clays, Fe-oxides, and carbonates. Not coincidentally, such compounds are also the most common host minerals for the microbial fossil record on Earth, and the classic microbiotas of the Precambrian are almost exclusively preserved in such lithologies. Other aqueous minerals, including a wide variety of evaporite minerals (salts), and even ice, also provide excellent media for preserving microorganisms. However, an important caveat with these classes of minerals is that residence times in the Earth's crust tend to be quite short (hundreds of millions of years for evaporites owing to dissolution and hundreds of thousands of years for ice due to long-term climatic warming). However, it is quite likely that residence times for aqueous mineral deposits on Mars will be different. The hydrological cycle on Mars appears to have died very early and evaporites may yet persist there as surficial deposits in paleolake basins. But the chaotic obliquity of Mars suggests that the present martian chryosphere is likely to be very young owing to periodic global warming and therefore unlikely to hold evidence of an early biosphere. Nevertheless, the present martian ice caps could be an important source of information about extrinsic inputs of organics (e.g., IDPs or cometary impacts) during the recent history of the planet.

The basic criteria outlined above suggest that the long-term preservation of a fossil record on Mars is likely to have occurred in a comparatively small number of geologic environments. The oldest

terraces on Mars, those formed during the early wet period, offer the greatest interest for exopaleontology. However, the discovery of favorable paleoenvironments on Mars will require a more detailed knowledge of the surface geology and mineralogy of the martian surface. Unfortunately, we have yet to determine the mineralogy of martian surface or even identify one aqueous mineral deposit there with any certainty. Thus, a first step in implementing a strategy for Mars exopaleontology is the identification of aqueous mineralogies on the surface.

High-Resolution Orbital Imaging in 2001: As noted above, perhaps the most basic requirement for implementing a strategy to explore for an ancient biosphere on Mars is the identification of key geologic environments and aqueously deposited mineralogies from orbit [4]. In order for the proposed 2005 sample return to legitimately address the concerns of exopaleontology, rock samples of appropriate mineralogy should be returned from a yet to be identified high-priority site in the southern highlands of Mars. Given the coarse spatial resolution of the Thermal Emission Spectrometer (TES) that will be flown in 1996 (3 km/pixel [7]), it will likely prove difficult to resolve the precise spatial location of target mineral deposits. In addition, at the scale mapped, each pixel of TES data is likely to involve a complex mixture of mineralogies, and deconvolution of discrete mineral spectra may likewise prove difficult to impossible. Obviously, the solution to such problems is higher-spatial-resolution data from orbit or high altitude. Therefore, in order to optimize site selection for samples of exopaleontological interest during the 2005 sample return, high-resolution (100 m/pixel) compositional mapping is deemed essential.

It is unlikely that a mid-IR orbital instrument that can achieve an acceptable signal-to-noise ratio within existing cost/weight guidelines, and therefore it is recommended that high-spatial-resolution data be obtained using a near-IR (1–5- μm range) hyperspectral (10-nm bandwidths) imaging system to create maps of high-priority target areas for future landed missions. The technologies needed to accomplish this task are relatively mature, because near-IR mineral mapping is a standard exploration tool in the minerals industry. High-resolution data obtained from orbit will not only provide a basis for detailed site studies for future landed missions, but will also yield valuable information that will assist the interpretation of data obtained by the TES during its global mapping exercise (e.g., deconvolution of mineral spectra and precise spatial location of deposits of interest).

In order to use high-resolution mineralogical mapping to assist with site selection for a 2005 sample return, it should be obtained during the 2001 opportunity. However, we do not recommend the substitution of an orbital for landed mission in 2001, because a lander in 2001 will be needed to prepare for landed science in both 2003 and 2005.

Balloon Missions: A high-priority mission proposal that presently lies outside the MGS program is a midlatitude aerobot/balloon mission to Mars that would carry a high-spatial-resolution mid-IR spectral imager. This would facilitate the mapping of surface mineralogy at the desired 100 m/pixel spatial resolution, while providing highly resolved spectral data to assist in interpreting the global TES dataset. Optimally, the spectral range of this instrument should be in the 5–12- μm range, where many fundamental vibrations of high-priority aqueous minerals (e.g., carbonates, silica, evaporites) can be detected. It would be preferable from the standpoint of exopaleontology to deploy such a mission over southern

highland terranes at a latitude that would transect several high-priority targets.

Landed Missions: Obviously, exobiological site recommendations for future landed opportunities will necessarily reflect a balance of programmatic goals. But to achieve maximum science return for exopaleontology, certain milestones (listed below) should be met during precursor landed missions in 2001 and 2003.

Mobility. The rover in 2003 should be capable of multiple-kilometer traverses during nominal mission times to provide access to a broad sampling of geologic targets at a site of exopaleontological interest.

Sample selection. Rovers for 2001 to 2005 should be able to survey rock fields and preselect individual target rocks for *in situ* analysis and (in 2005) sample return based upon mineralogy. This capability will require high-resolution visible range cameras and a rover-mounted (preferably mid-) IR spectrometer.

Microscopic imaging. Once targets have been identified, rovers should be able to image weathered and fresh rock surfaces at "hand lens" magnifications (0.1 mm resolution) in order to visualize microtextures of rocks. Optimally, illumination systems for rover hand-lenses should deliver visible, infrared, and UV wavelengths to assist in textural and compositional evaluation. UV could be particularly valuable because many minerals and organic materials autofluoresce and exhibit unique spectral signatures.

Access to rock interiors. Rovers should have the ability to access rock interiors by exposing fresh surfaces either through breakage or abrasion. This capability is regarded as a key requirement for all analytical tools that seek to evaluate composition.

***In situ* mineralogical analysis.** Although elemental analysis is regarded as important for exopaleontology in providing information about the biogenic elements, in order to address the important issues of exopaleontology instrument payloads must also provide information about molecular structures that will lead to an understanding of mineralogy. Key technologies for mineralogical analysis include more qualitative tools, such as IR spectroscopy and laser raman, which operate in a reflected energy mode, and more definitive methods, such as X-ray diffraction, which, using the optimal transmission mode geometry, require a powdered sample.

Redox analysis. In order to optimize the recognition of samples likely to preserve organic matter, instrumentation should provide capability for determining the oxidation state of iron in potential rock samples. The various mineralogical instruments described above provide important tools for evaluating redox, and Mossbauer is especially effective for iron-bearing minerals.

Site Selection: Because only selected areas will be mapped at high resolution during upcoming orbital missions, targets for high-resolution imaging should include high-priority sites for exopaleontology. A catalog of such sites is being assembled to assist mission planners [8]. Although there are a number of geological sites of potential exopaleontological interest [9], the most easily identified targets from orbit are most likely to be those within ancient paleolake basins in the southern highland terranes of Mars [6]. Such sites may provide access to a variety of aqueous mineralogies, including fine-grained, aqueously deposited detrital sediments (e.g., claystones and shales) and mineral precipitates such as evaporite deposits, spring-deposited carbonates, and more broadly distributed sedimentary cements.

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Viewgraphs presented at meeting—

Background

Post-Viking view of Mars Exobiology emphasizes exploration for an ancient biosphere

Requires a distinctly different conceptual framework, strategy, and methodology (=exopaleontology)

Conceptual Framework and Strategy

Strategy incorporates information from Precambrian paleontology, microbial biosedimentology and biogeochemistry, and studies of modern and ancient analogs

Important Connections

The detection of prebiotic and/or biological signatures in rocks is intimately connected to the search for a volatile/paleoclimate record and mineral resources

Core Principles

Preservation of biological signatures in rocks depends on organisms and their byproducts being rapidly entombed by fine-grained (impermeable) mineral phases that have long crustal residence times

Creating a Balanced Program of Exploration

Given the focus of the Global Surveyor Program (life, volatiles, resources) and the need to balance these goals within the context of upcoming missions, it is essential that key exobiological milestones be addressed in a timely manner

Exobiological Milestones

Discovery of target deposits (aqueously deposited minerals and/or fine-grained sediments based on spectral mapping from orbit or altitude)

Rover-based sample selection and preparation to detect organic compounds in target deposits (simple presence-absence followed identification of specific compounds and chirality)

Detection of possible biofabrics in rocks (visualization of microstructures in rocks at 10–50× magnifications using rover “hand-lens”)

Isotopic analysis of key minerals (those that could have been influenced by biological processes) and organic matter

Return of targeted lithologies to Earth for detailed analysis using a variety of more sophisticated methods

Detection of “fossils” in the broad sense (chemical or morphological fossils and biominerals)

How do we locate targets?

“Top-down” approach required with progressive narrowing of focus to key sites

Locate geologic terranes and aqueous mineral targets from orbit

Requires high-spatial-resolution (hundreds of meters to kilometers per pixel) spectral mapping

Spectral ranges:

Near-IR 1.0–3.0 μm

Mid-IR 5.0–12.0 μm

Reaching Targets

Rovers capable of multiple-kilometer traverses in 2003

Precision landing to <5.0 km improving to hundreds of meters accuracy by 2005

Exobiological Milestones Addressable Within Surveyor Program

Detection of target deposits from orbit (1996, 1998?, 2001, 2003)

Detection of key mineralogies during landed missions (site selection based on orbital mapping in 1996–1998 and landed missions in 2001 and 2003)

Visualization of microscale fabrics in rocks (1998 lander? Rover-based reflected light microscopy in 2001 and 2003)

Detection of organic compounds (assuming sample selection and preparation capabilities for landers, 2001 and 2003)

Return of targeted lithologies (those with good potential for having captured and retained biosignatures) in 2005 (site selection!)

Steps in the Search for Prebiotic Chemistry or Ancient Biosignatures

Detection of targets from orbit or altitude (balloon): Need for high-resolution infrared spectroscopy

Deliver landers and rovers within reachable distances of targets: Need for precision landing systems

Rover mobility determined by science goals, size of landing ellipse, target sizes

Access to the right kinds of target lithologies (unweathered, unoxidized): Need rock drills and sample delivery systems

In situ analysis for organics (simple presence-absence followed by identification of specific compounds)

Exobiological Inputs to Upcoming Missions

Pathfinder mission site selection: Site selected reflects combined goals and has potential to capture an exobiological milestone—namely, the detection of aqueous mineralogies

Selection of targets for high-resolution imaging during MGS '96 (MOC and TES)

Suggest flying a hyperspectral, high-spatial-resolution IR spectrometer in 2001 to assist interpretation of TES data and with targeting site for 2003 lander and sample return in 2005

Selection of site for 2005 sample return (and 2003 if the same) should reflect the joint goals of life, volatiles, climate, and resources (geology)

At the "Bottom Line"

If we wish to retain the search for past/present life as an objective in the program, exobiological milestones need to be addressed at each opportunity. At this stage of Mars exploration, these milestones are complimentary to those of other disciplines (volatiles and climate, resources or geology).

Achieving the goals of the exobiology community will require a long-term view of the problem and a phased plan of exploration. Decision trees are a realistic way to assess present needs and to benefit from future missions.

Timely progress in achieving milestones identified will ensure we are moving ahead at each opportunity in meeting what the Agency (and public!) regards as an essential element of the program.

It is clear that life-related issues must be handled carefully as they are presented to NASA and the public to not create an imbalance, or more importantly, misunderstanding about where we are in the exploration plan.

55-91

057172

Jeffrey L. Bada, Scripps Institution of Oceanography—

Detection of Amino Acids on Mars

The unambiguous detection of amino acids on Mars would be of pivotal importance in the understanding of the processes involved in the origin of life. Homochirality would be the best indicator of whether any detected martian amino acids were biotic or abiotic in origin. Several possible methods could be used *for in situ* amino acid analyses on Mars, but capillary electrophoresis would likely be the most suitable because it can be easily miniaturized and has small reagent and power requirements. Returned samples could be analyzed by any method then in routine laboratory use, but terrestrial contamination could interfere with the detection of trace levels of endogenous martian amino acids.

Introduction: Understanding the events that led to the origin of life on Earth is complicated by the lack of geological evidence around 4 b.y. ago, when the transition from prebiotic chemistry to biochemistry likely took place. Although erosion and plate tectonics have erased the terrestrial geological record at the time of the origin of life, there is a possibility that information about this period of Earth history may be still preserved on Mars. Compared to Earth, Mars is a much more placid planet; there is no known plate tectonic activity, and surface alteration rates are minimal. Extensive areas of the martian surface may date to >4 b.y. ago [1,2]. Geomorphological evidence suggests that liquid water existed on the martian surface at some point in the past, and early Mars may have had an atmosphere similar to that of the early Earth [3]. If this is the case, then at least some of the steps leading to the origin of terrestrial biochemistry may have also taken place on Mars [4]. Thus, traces of prebiotic chemistry, or biochemical evidence associated with extinct martian biota, could be present on Mars. Though deemed unlikely, life may even still exist today on Mars in some protected subsurface environments [5,6].

The processes thought to be involved in the origin of life on Earth are summarized in Fig. 1. The first requirement is the presence

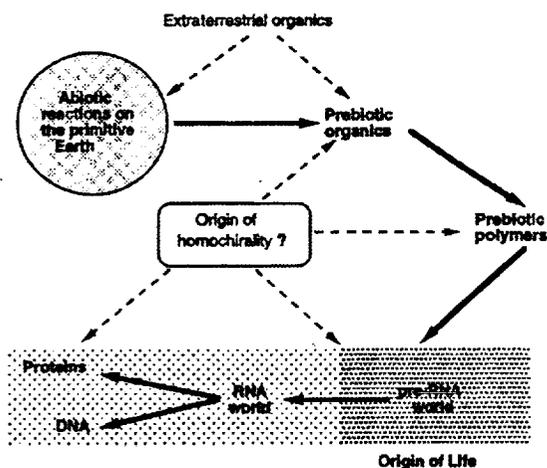


Fig. 1. A generalized diagram showing the various steps involved in the origin of life. Life is defined as an autonomous replicating system that evolves by natural selection.

of a prebiotic soup consisting of a rich variety of organic compounds, although at this point we do not know the soup composition necessary for the origin of life. The components of the soup may have been made directly on Earth, or supplied from space by comets, asteroids, micrometeorites, or interplanetary dust particles [7]. A large variety of organic compounds, including those that play a major role in biochemistry such as amino acids, purines, pyrimidines, etc., have been identified in one class of meteorites, the carbonaceous chondrites (Fig. 2). Besides demonstrating that important biomolecules can be produced abiotically in extraterrestrial environments, their presence also suggests that exogenous compounds should be periodically delivered to the surface of the Earth (and other planetary bodies as well) by various delivery processes [7]. The subsequent transition from the abiotic chemistry of the primitive Earth to the first self-replicating molecular systems capable of Darwinian evolution marked the point of the origin of life. On the Earth, subsequent evolution of the first self-replicating molecules then gave rise to the RNA world and finally the DNA/protein world characteristic of all life today.

The surface of Mars could hold clues about the various processes and stages involved in the origin of life. A major goal of the NASA Space Exploration Program over the next several decades is to search for evidence of extinct and extant life, and abiotic chemistry, on Mars. During the next decade, spacecraft will orbit Mars and land on the surface. Within 15 years, sample return missions are planned that will provide scientists with material to analyze directly in the laboratory. An important consideration of these efforts is what compounds we should search for, either directly on Mars or in martian samples returned to Earth, that will answer unambiguously whether abiotic and/or biotic organic molecules are present.

Previous Organic Analyses of Mars: The detection of organic material on the martian surface was attempted by the Viking 1 and 2 landers in 1976. These spacecraft each carried a gas chromatograph coupled to a mass spectrometer [9-11]. No organic compounds were detected above the part per billion (ppb) level in the upper few centimeters of the martian surface. The results of other experiments on board the landers, however, led to the conclusion that the martian surface is saturated with an oxidant of unknown type, and thus any organics deposited in the martian surface layer would be destroyed on short timescales [12]. The oxidizing layer

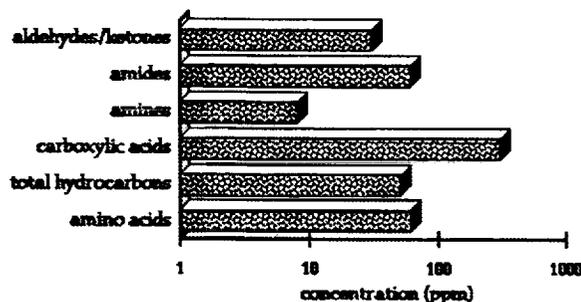


Fig. 2. A summary of the various organic compounds detected in carbonaceous chondrites. Taken from [8].

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may only extend a few meters below the surface, however [13], so the preservation of martian organics in the subsurface is possible [14].

Aside from these Viking missions, the only other opportunities to directly analyze martian samples have come from the SNC meteorites, which are fragments of the martian crust ejected by impact events that eventually found their way to Earth [15]. The Antarctic shergottite EETA 79001 has been of considerable interest because it contains a carbonate component with 600–700 ppm combustible carbon, which has been suggested to be endogenous martian organic material [16]. Analyses of a small fragment of the EETA 79001 carbonate material detected only the L-enantiomers of the amino acids found in proteins [17]. There is no indication of the presence of α -aminoisobutyric acid (Aib). Aib is a common amino acid in carbonaceous meteorites and is readily synthesized in laboratory-based prebiotic experiments, but is not one of the amino acids found in the proteins of terrestrial organisms [18]. The amino acids in this martian meteorite are thus terrestrial contaminants derived from Antarctic ice meltwater that had percolated through the meteorite [17]. Failure to detect extraterrestrial amino acids in this martian meteorite does not rule out the possibility of endogenous amino acids on Mars because the severe conditions experienced during impact ejection should have destroyed any amino acids that were originally present. These results do suggest, however, that the transfer of organic material from Mars to Earth, or vice versa, by impact ejecta appears unlikely.

What Molecules Should We Search for During Future Mars Missions? Any strategy for investigating whether organic molecules are present on Mars should focus on compounds that are readily synthesized under plausible prebiotic conditions, are abundant in carbonaceous meteorites, and play an essential role in biochemistry. One of the few classes of molecules that fulfill all these requirements are amino acids, although we do not know whether amino acids were a component of the first self-replicating systems, or even required for the origin of life. Amino acids are synthesized in high yields in prebiotic experiments [18], are one of the more abundant types of organic compounds present in carbonaceous meteorites (see Fig. 2), and are the building blocks of proteins and enzymes. Amino acids are ubiquitous molecules on the surface of the Earth [18], and it is likely that regardless of whether they are of abiotic or biotic origin, they would be widespread on the surface of Mars as well.

A central problem in future organic analyses of martian samples is not only identifying and quantifying organic compounds that may be present, but also distinguishing those molecules produced abiotically from those synthesized by extinct or extant life. Terrestrial biology uses only a small subset of the large variety of amino acids, nucleic acid bases, and sugars that can be synthesized abiotically and would have thus possibly been present in the prebiotic soup. The detection on Mars of a limited number of the total array of possible organic molecules of biological importance could be suggestive of biochemistry, but that criteria alone would be weak evidence. The most reliable indicator of the biological vs. abiotic origin of organic molecules is molecular homochirality [19]. Terrestrial organisms use almost exclusively L-amino acids (the L-enantiomer) in protein biosynthesis, and D-ribose and D-deoxyribose in nucleic acids. The structural principles on which biomacromolecule activity is based lead us to believe that any functional biochemistry must use a single enantiomer of any molecule that possesses a chiral carbon. In con-

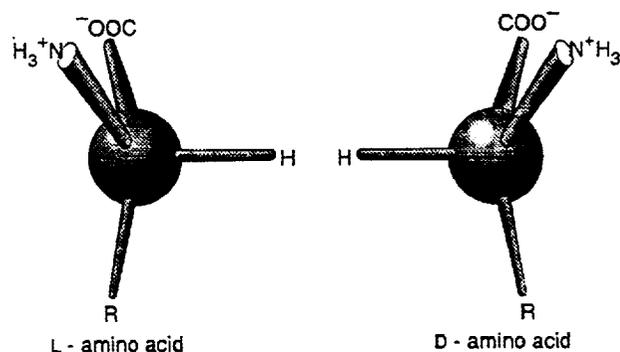


Fig. 3. A sketch of L- and D-amino acids. Equal amounts (a racemic mixture) of lefthanded (L) and righthanded (D) amino acids are synthesized in abiotic experiments, but life on Earth uses only one type—L-amino acids.

trast, all known laboratory abiotic synthetic processes result in racemic mixtures of organic compounds with chiral carbons, and the amino acids in carbonaceous chondrites are also racemic [19].

Amino acid homochirality provides an unambiguous way of distinguishing between abiotic vs. biotic origins (Fig. 3). In terrestrial organisms, amino acid homochirality is important because proteins cannot fold into bioactive configurations such as the α -helix if the amino acids are racemic. Enzymes likely could not have been efficient catalysts in early organisms if they were composed of racemic amino acids. However, enzymes made up of all D-amino acids function just as well as those made up of only L-amino acids, but the two enzymes react with the opposite stereoisomeric substrates [20]. There are no biochemical reasons why L-amino acids would be favored over D-amino acids. On Earth, the use of only L-amino acids by life is likely simply a matter of chance. We assume that if proteins and enzymes were a component of extinct or extant life on Mars, then amino acid homochirality would have been a requirement. However, the possibility that martian life was (or is) based on D-amino acids would be equal to that based on L-amino acids.

As can be seen in Table 1, the detection of a nonracemic mixture of amino acids in a martian sample would be strong evidence for the presence of an extinct or extant biota on Mars. The finding of an excess of D-amino acids would provide irrefutable evidence of unique martian life that could not have been derived from seeding the planet with terrestrial life. In contrast, the presence of racemic amino acids, along with abiotic amino acids such as Aib, would be indicative of an abiotic origin, although we have to consider the possibility that the racemic amino acids were generated from the racemization of biotically produced amino acids [18].

TABLE 1. Amino acids as indicators of abiotic and/or biotic chemistry on Mars.

Abiotic Chemistry	Presence of nonprotein amino acids α -aminoisobutyric acid and racemic isovaline*
Extinct Life	Amino acids with different amounts of racemization*†
Extant Life	Amino acid homochirality*†

* Possible now with SNC meteorites

† Future Mars mission

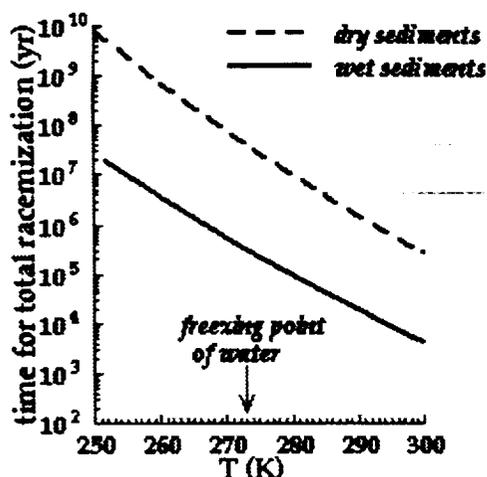


Fig. 4. Time (yr) for total racemization of aspartic acid in dry and wet sediments as a function of temperatures relevant to Mars throughout its history. Taken from [2].

When an organism dies, its amino acids begin to racemize at a rate that is dependent on the particular amino acid, the temperature, and the chemical environment [18]. Racemization reactions are rapid on the terrestrial geologic timescale and even at deep ocean temperatures of 2°C; amino acids are totally racemized (e.g., D/L = 1.0) in about 5–10 m.y. Using kinetic data, the racemization half-lives and times for total racemization of aspartic acid, a common protein amino acid, under conditions relevant to the surface history of Mars have been estimated (see [21] and Fig. 4). Amino acids from an extinct martian biota maintained in a dry, cold (<250°K) environment would not have racemized significantly over the lifetime of the planet (4.5 b.y.). Racemization would have taken place in environments where liquid water was present even for time periods of only a few million years following biotic extinction. The best preservation of amino acid homochirality associated with extinct martian life would be in the polar regions. When biogenic amino acids are completely racemized, they would be indistinguishable from a chirality point of view from the racemic amino acids produced by abiotic organic synthesis or those derived from exogenous sources. Although α -dialkyl amino acids with a chiral center, which are common in carbonaceous meteorites [8], are very resistant to racemization [18], these amino acids are not generally found in the proteins of terrestrial organisms. However, we cannot exclude the possibility that α -dialkyl amino acids might not be used by life elsewhere. The finding on Mars of racemic amino acids of the type found in the proteins of terrestrial organisms along with the presence of nonracemic α -dialkyl amino acids would suggest that life did or still does exist.

Amino Acid Detection Methodologies on Mars: In Table 2, we have evaluated the spacecraft worthiness of various amino acid analytical methods in routine use in the laboratory today that might be used to carry out *in situ* analyses on the surface of Mars. In general, the three methods—gas chromatography coupled with mass spectrometry detection (GC/MS), high-performance liquid chromatography (HPLC), and capillary electrophoresis (CE)—appear to be about equally suitable for spacecraft instrumentation. However, the prospects for miniaturization make CE probably the best choice.

TABLE 2. Amino acid analysis techniques currently in routine laboratory use.

	Suitability index for spacecraft operation:			
	less suitable	more suitable		
	1	2	3	
		GC/MS*	HPLC†	CE‡
Sensitivity	1	3	2	
Run time	1	2	3	
Weight	2	1	3	
Mechanical complexity	2	1	3	
Buffer volume and storage	3	1	2	
Ease of derivatization	1	3	1	
Confirmation of peak identity	3	1	1	
Proven space worthiness	3	1	1	
Enantiomeric resolution	2	3	3	
Total score	18	16	19	

* Gas chromatography/mass spectrometry.

† High-performance liquid chromatography.

‡ Capillary zone electrophoresis.

GC/MS is an obvious method for molecular organic analysis from a landed martian spacecraft, because of the success with similar instrumentation during the Viking missions. Any GC/MS spacecraft system for future missions, however, must be able to distinguish abiotic vs. biotic origin through enantiomeric resolution. Either chemical derivatization procedures that produce diastereomeric derivatives, or a chiral stationary phase that can separate derivatized enantiomers, would be required. These procedures require additional hardware such as reaction chambers, valves, and pumps, and can greatly increase the size, weight, and mechanical complexity of the GC/MS system. Commonly used GC detectors besides MS such as thermal conductivity detectors likely lack the sensitivity needed to detect amino acids at the sub-parts per billion level, a necessity that should be a requirement for exobiological analysis on Mars. Flame ionization detectors have greater sensitivity, but would probably be too unstable and dangerous for spacecraft use.

HPLC is somewhat more suited to chiral amino acid analysis. Simple chiral derivatization procedures exist for HPLC, and fluorescence detection can be used to achieve sensitivities well below the parts per billion level. Reverse-phase HPLC with *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization and fluorescence detection has been used to search for extraterrestrial amino acids in meteorites [17] and lunar samples [22], in sediments from the Cretaceous/Tertiary boundary [23], and in polar ice core samples [24]. HPLC hardware, however, is heavy and mechanically complex and requires large volumes of solvents. These are all disadvantages when designing instrumentation for spacecraft use.

A relatively new technology that shows promise for spacecraft-based amino acid analysis is microchip-based capillary electrophoresis [25,26]. CE can use the same chiral derivatization reagents (such as OPA/NAC) and sensitive detection techniques (such as laser-induced fluorescence) as HPLC. The actual separation hardware, including buffer reservoirs and derivatization reaction chambers, can be etched onto glass microchips with dimensions on the order of centimeters. Such a system has great advantages over GC or HPLC systems in weight and size. The reagents, sample, and

solvents can also be manipulated using the electro-osmotic forces that effect the separation, with no need for mechanical pumps or valves. Sensitive detection systems such as laser-induced fluorescence or electrochemical detection [27,28] can be used in a microchip CE system to achieve sub-parts per billion detection limits. Microchip capillary electrophoresis appears to be the best currently available technique for the *in situ* enantiomeric resolution of optically active compounds in extraterrestrial samples.

Amino Acid Detection in Martian Samples Returned to Earth: A complete evaluation of the inventory of the organic compounds that may be present on Mars will require returned samples, especially if prior *in situ* analyses yield any positive results. Future martian samples returned to Earth could be analyzed, in theory at least, by any suitable analytical technique then in existence. However, there are limitations in returned sample analyses. The cost of a sample return mission may limit at least initially sampling to only a few geologically distinct sites on Mars. The size of sample that can be returned using presently available space transportation technology may limit the number of laboratory-based analyses that can be performed, and may even eliminate techniques with large sample requirements. Compound-specific organic analyses of a returned martian sample might be limited to techniques that are compatible with other areas of investigation, such as mineralogy and stable isotope analyses.

However, the main limitation of organic analyses of samples returned from Mars will be the omnipresent problem of terrestrial contamination. Even the best and most sensitive analytical methodologies used today must deal with contaminants in reagents, etc., that limit the detection of extraterrestrial organic compounds. Although this could also be a potential problem for *in situ* martian analyses, there are ways that this might be minimized. Any spacecraft landed on the martian surface would be required to undergo rigorous decontamination in order to ensure that the planet is not inoculated with terrestrial organisms. Reagents used for *in situ* analytical systems would thus be extensively purified prior to the mission and probably transported dry. Water required for aqueous buffers and sample processing could be made, or condensed from the atmosphere, directly on the martian surface.

Terrestrial contamination has limited the detection of Aib in lunar soils to about 0.1 ppb [22] and to around 1 part-per trillion (ppt) in polar ices [24]. As an example of the contamination problem, consider the analyses of small samples of the organic-rich Murchison meteorite shown in Fig. 5. Although the extraterrestrial amino acid Aib is clearly detectable in the 10-mg sample, in the 100-mg sample Aib is almost completely obscured by interfering peaks. Using a value of 10 ppm for the Aib content of Murchison [22], the Aib detected in the 100-mg sample corresponds to about 1 ng (10^{-9} g). Thus, in order to detect extraterrestrial amino acids such as Aib at the parts per billion level would require at least 1 g of a martian sample. This is would likely be considered a "large" sample, and samples could be restricted to much smaller amounts. Thus, in order to detect trace levels of amino acids in samples of Mars returned to Earth, the background contamination from terrestrial amino acids and other interfering compounds would need to be greatly reduced. Because any returned sample from Mars would be quarantined in order to ensure that any martian organisms present did not contaminate the Earth, facilities could be set up as well to prepare superclean reagents, etc., that would be necessary to reduce terrestrial background organic levels.

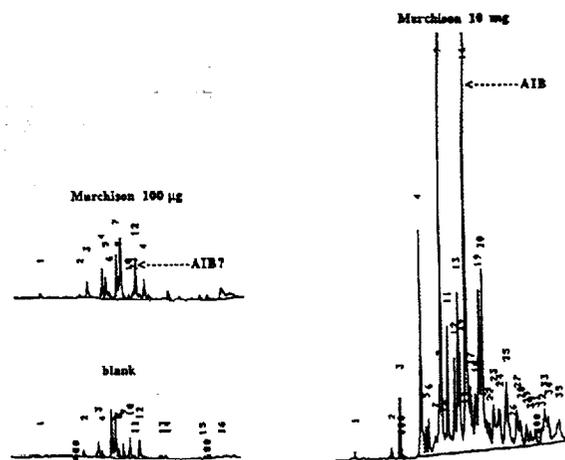


Fig. 5. Analyses of small samples of the Murchison meteorite using HPLC with OPA/NAC derivatization and fluorescent detection (see [23] for description of analytical method). The peaks corresponding to Aib are indicated. Aib in the 100- μ m sample is nearly obscured by interfering peaks.

Future Prospects: The next couple of decades will be exciting times with respect to the question of whether life existed or exists elsewhere in the solar system and the resolution of the problem of how life originated on Earth. The exploration and the organic analyses of the surface of Mars will undoubtedly be of pivotal importance. State-of-the-art analytical chemical techniques will play a major role in these endeavors. Finding evidence of extinct life on Mars would be, to put it mildly, sensational. The presence of extant life on Mars could be even more so, and would revolutionize our understanding of the chemistry of life. We can hardly wait!

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56-91
057173**David J. Des Marais, NASA Ames Research Center—****Searching for Biogeochemical Cycles on Mars**

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The search for life on Mars clearly benefits from a rigorous, yet broad, definition of life that compels us to consider all possible lines of evidence for a martian biosphere. Recent studies in microbial ecology illustrate that the classic definition of life should be expanded beyond the traditional definition of a living cell. The traditional defining characteristics of life are threefold. First, life is capable of metabolism, that is, it performs chemical reactions that utilize energy and also synthesize its cellular constituents. Second, life is capable of self-replication. Third, life can evolve in order to adapt to environmental changes. An expanded, ecological definition of life also recognizes that life is a community of organisms that must interact with their nonliving environment through processes called biogeochemical cycles. This regenerative processing maintains, in an aqueous conditions, a dependable supply of nutrients and energy for growth. In turn, life can significantly affect those processes that control the exchange of materials between the atmosphere, ocean, and upper crust. Because metabolic processes interact directly with the environment, they can alter their surroundings and thus leave behind evidence of life. For example, organic matter is produced from single-carbon-atom precursors for the biosynthesis of cellular constituents. This leads to a reservoir of reduced carbon in sediments that, in turn, can affect the oxidation state of the atmosphere. The harvesting of chemical energy for metabolism often employs oxidation-reduction reactions that can alter the chemistry and oxidation state of the redox-sensitive elements carbon, sulfur, nitrogen, iron, and manganese.

For example, rates of interconversion between sulfate and sulfide are greatly accelerated by life's energy harvesting processes. Sulfate and sulfide are widely distributed between Earth's atmosphere, ocean, crust, and mantle. At temperatures $>250^{\circ}\text{C}$, sulfides and sulfates exchange readily via thermal processes. However, abiotic exchange processes are very slow below 200°C . Biological processes catalyze this exchange at lower temperatures, thus life dominates the exchange of sulfide and sulfate under the conditions prevailing at Earth's surface. At equilibrium, sulfate is ^{34}S -enriched, relative to sulfide. This isotopic difference increases at lower temperatures, therefore biologically mediated isotopic exchange between sulfate and sulfide is characterized by a large scatter of $^{34}\text{S}/^{32}\text{S}$ values in crustal reservoirs of sulfide and, to a lesser extent, sulfate. Therefore this scatter of $^{34}\text{S}/^{32}\text{S}$ values observed in ancient sedimentary rocks is a legacy of life and constitutes solid evidence for its existence.

The budget of carbon in crustal sedimentary rocks also has been substantially influenced by the biosphere. Approximately 20%

of crustal carbon is stored as organic matter. The size and chemical composition of this organic reservoir has been fixed by the oxidation state of Earth's mantle, tectonic processes affecting the crust, and life. If the synthesis and burial of organic carbon had not occurred, substantially less organic matter would have been stored in the crust.

Our concepts as to how evidence of life might be found on Mars is influenced strongly by our understanding of the environmental limits for life on Earth. Temperature, liquid water, and the availability of chemical or light energy appear to be crucial parameters. Our understanding of these limits has been extended recently. For example, life in hydrothermal systems extends up to at least 117°C . The discovery of life in ancient aquifers in the Columbia River plain illustrates that ecosystems can thrive on the basaltic weathering reactions in complete isolation from the surface environment. Both of these findings indicate that life could have persisted in the martian subsurface for perhaps millions to billions of years.

Our understanding, both of life's ultimate capacity for survival and of its impact upon crustal composition, makes our search for a past or present martian biosphere much more effective. Our definition of a "fossil" must be expanded beyond its traditional limits. Microbial fossils can be preserved cellular structures, macroscopic mineral structures built by communities (e.g., "microbial reefs"), organic molecules, minerals whose deposition was biologically controlled, and stable isotopic patterns in elements such as carbon, nitrogen, and sulfur. The most convincing proof of fossils consists of multiple lines of evidence derived from several of these fossil types.

Have there ever been biogeochemical cycles on Mars? Certain key planetary processes can offer clues. Active volcanism provides reduced chemical species that biota can use for organic synthesis. Volcanic carbon dioxide and methane can serve as greenhouse gases. Thus the persistence of volcanism on Mars may well have influenced the persistence of a martian biosphere. The geologic processing of the crust can affect the availability of nutrients and also control the deposition of minerals that could have served as a medium for the preservation of fossil information. Finally, the activity of liquid water is crucial to life. Was there ever an Earth-like hydrologic cycle with rainfall? Has aqueous activity instead been restricted principally to hydrothermal activity below the surface? To what extent did the inorganic chemistry driven by sunlight and hydrothermal activity influence organic chemistry (prebiotic chemical evolution)? Our efforts to address these and other key questions will benefit greatly from the first samples returned from Mars.

Viewgraphs presented at meeting—

Biogeochemical Cycles on Mars?

Cycling of materials between reservoirs in the atmosphere, ocean, crust, and mantle

Timescales for cycling depend on reservoirs involved

e.g., fastest: atm.-ocean, slowest: crust-mantle

Life can significantly affect processes that link the atmosphere, ocean, and upper crust

Characteristics of Life

Metabolism

Energy harvesting

Synthesis of cellular constituents

Self-replication

Sustains all components required by theory

Evolution

Adaptation to environmental changes

Metabolism

Synthesis of cellular constituents

❖ e.g., organic synthesis from C1 precursors, intermediary metabolism (organic interconversions)

Energy transduction

Exploits external sources of free energy

❖ e.g., redox reactions, light harvesting

Overcomes kinetic barriers to reactions

Employs catalytic enzymes

❖ e.g., organic chemistry, inorganic redox reactions

Redox Reactions Accelerated by Life

Life affects atmosphere, ocean, and crust by altering the chemistry of C, N, S, H, P, etc.

Relative sizes of oxidized and reduced reservoirs

Reaction networks that bind the biogeochemical cycles together

Crustal chemistry becomes a legacy, therefore a clue, of the biosphere's history

Biogeochemical Sulfur Cycle

Sulfates and sulfides distributed between atmosphere, ocean, crust, and mantle

At $T > 200^\circ\text{C}$, sulfides and sulfates exchange via thermal processes

At $T > 200^{\circ}\text{C}$, life dominates exchange between sulfides and sulfates, as reflected in stable isotopic patterns

Wide scatter in sulfur isotope values in ancient sedimentary rocks is legacy of biosphere

Earth's Carbon Budget

Reservoir sizes vary substantially: biosphere and oceans \ll crust \ll mantle

Dominant crustal reservoirs: carbonates and organics

Enormous crustal organic reservoir is major legacy of our biosphere: its pervasiveness and its antiquity

Similar situation on Mars?

Biogeochemical Carbon Cycle

Size of crustal reservoir fixed by mantle-crust exchange; acting over long timescales

Size and composition of organic reservoir fixed by mantle redox, tectonics, and life; acting over intermediate timescales

Bimodal carbon isotopic pattern (organics vs. carbonates) is a legacy of biosphere

Range of Conditions that Sustains Life

Defined in three-dimensional space by environmental characteristics of temperature, water potential, and availability of energy

Due to recent advances in biogeochemistry, our estimation of this range of conditions has expanded

Defines the limit of the environments in which we can hope to find life; affects Mars strategy

Recent Examples Extending Life's Known Limits

Microbial floc exhaled by midocean ridge during eruption
Evidence for ecosystem within hydrothermal plumbing

Does biosphere extend to 150°C ? (now known to 117°C)

Microbial mats in Columbia River basalt aquifer
Community sustained by chemoautotrophs (methanogens)

Methanogens utilize products of basalt weathering, isolated from surface environment

Could life exist in Mars' subsurface, isolated from hostile surface?

Records of the Early Biosphere

Our understanding of biogeochemical cycles makes our search for ancient fossils much more effective

Types of fossils: microfossil cells, microbialites (community structures), biominerals, organic molecules, stable isotope patterns

Indicators of various components of biogeochemical cycles

Convincing confirmation of fossils requires evaluation of multiple lines of evidence (criteria) for biogenicity

Martian Biogeochemical Cycles?

Mantle/crust exchange (e.g., volcanism)

Maintenance of atmosphere/greenhouse

Source of free energy and reducing power for life

Crustal dynamics (tectonics)

Maintains habitable environments (energy, nutrients)

Controls preservation of ancient environmental record

Aqueous activity (transport, chemistry)

Ancient "Earth-like" hydrologic cycle?

Hydrothermal systems—"oases"?

Chemical evolution, extinct or extant life?

❖ Coupling between inorganic and organic reactions?

Conditions that could Sustain Life on Mars

Within "biozone" defined by water, temperature, and energy

Ancient Mars: Perhaps included both surface and near-subsurface

Today: Perhaps only includes subsurface zone: from ~1 km to a few kilometers down?

Evaluation of these zones for exobiology equates to evaluating their potential for sustaining biogeochemical cycles

Martian Biogeochemical Samples

Define geochemical cycles of biogenic elements

Reservoir sizes, composition, locations

Nature of processes linking the reservoirs

Specific issues for chemical evolution/exopaleontology

Sources of greenhouse gases and reducing power

Agents for regenerating nutrients, water, and bioenvironments

Integrated effects of liquid water: e.g., aqueous mineralogy

Organic chemistry

Returned samples

Sample very ancient and subsurface (~1 km) environments

Seek evidence of aqueous activity

Obtain diverse rock types (sample the geochemical cycles)

Climate History

Michael H. Carr, U.S. Geological Survey—

Sample Return and Climate

Understanding the climate history of Mars is essential for unraveling the geologic history of the planet and assessing its potential for biologic evolution. Suspicion that climates in the past have at times been very different from those that presently prevail is based largely on surface morphology, particularly the presence of the seemingly water-worn valley networks. The climate history is, however, very uncertain because of ambiguities in both the geomorphic interpretations and the ages of the relevant features. Possibly the strongest evidence for climate change is the unambiguous change in erosion rates at the end of heavy bombardment. Many Noachian craters tens of kilometers across are highly degraded, suggesting erosion rates comparable to terrestrial rates. In contrast, craters only a few kilometers across that formed after the Noachian are mostly well preserved, suggesting that erosion rates dropped by two to three orders of magnitude at the end of the Noachian. The evidence for climate change from the valley networks is less clear. Noachian units are the most heavily dissected. Over 70% of the valleys are incised into materials of this age. But the valleys continued to form throughout Mars' history as shown by the dissection of young volcanos. The general consensus is that the valley networks formed by slow erosion of running water. If so, then warm climates must have occurred late in Mars' history. But many attributes of the valleys suggest that other processes, such as small floods and mass wasting, may have contributed to their formation so that the evidence for climate change from the valleys, while suggestive, is not compelling. The large floods are also of climatologic interest for they indicate the presence on the planet of large amounts of water, and these very large events may have induced changes in climate. Modeling studies show that it would have been very difficult to induce major climate changes on early Mars because of the lower energy output of the Sun. These studies suggest that cloud formation in a CO₂/H₂O atmosphere would prevent significant greenhouse warming at the surface. Later in Mars' history a 3–5-bar CO₂ atmosphere could raise surface temperatures above 273 K and so allow liquid water at the surface. Carbonate deposits have not been detected, however, and these should be close to the surface if thick atmospheres had been present late in Mars' history. Thus the climate history of Mars is extremely uncertain.

Many of the uncertainties could be resolved with returned samples. Samples of the atmosphere, the regolith, and the rock record would all contribute. The atmosphere contains a record of its origins, subsequent additions, exchange with the surface, and losses to various sinks such as space and carbonate deposits. The record is mostly in the isotopic composition of the noble gases and various atmosphere elements such as C, N, and O. Losses to space appear to have been the dominant factor in setting the isotopic composition of the present atmosphere, but other processes have clearly been involved. Precise determination of composition of the present atmosphere will allow more precise determination of its evolution. The

composition is important in itself and also as a reference against which to compare the same gases trapped in polar deposits, weathering products, ancient glasses, and so forth. For the first sample return, elaborate sample mechanisms are not needed. Gases trapped in the head space of containers for other materials will be adequate.

The regolith must also contain information on climate. The source of the fine-grained air-deposited materials at the two Viking landing sites is not known. It is thought to be largely weathered material, but there must be other components such as volcanic dust and meteoritic debris. Because of the low erosion rates, and by inference low weathering rates, throughout Mars' history, the weathered material is suspected to have mostly originated early in Mars' history. Some indication as to whether this is true may be shown by model ages for the weathered materials. The chemistry and mineralogy of the regolith materials will provide us with indications of past climatic conditions. Weathering involves chemical interaction of the atmospheric species with silicate rocks. The isotopic composition of the weathered products therefore have the potential for indicating the isotopic composition of the atmosphere at the time of weathering. D/H and O isotopes are of particular interest. A seemingly salt-rich layer, or duricrust, was observed at both Viking landing sites. The layer indicates that vertical migration of salts has taken place within the soil profile. It is not clear that this migration can occur under present conditions, although it might, so the duricrust may provide information on climatic excursions that have taken place since the regolith materials were deposited. The requirements for a regolith sample on the first mission could be very simple. One to two scoops, amounting to 100 g, should be adequate. The soil could also be used as a filler in rock-sample containers. Vertical profiles through the duricrust could be acquired on subsequent missions.

Three main types of rocks are probably available for sampling: igneous rocks, breccias, and sediments. For climate studies igneous rocks are probably the least desirable. They may, however, contain information on weathering subsequent to deposition and on the composition of rock-altering fluids. They can also be used to calibrate the crater ages, thereby enabling the dating of events of climatological interest, such as large floods. Impact breccias from the era of heavy bombardment are of considerably more interest. They date from the era for which we have the best evidence for climate change. They consist of clasts of different types of rocks, and so provide a means of sampling the diversity of Noachian rocks, which could include sediments. Moreover, impacts can implant contemporary atmospheric gases in rocks, so that the breccias may provide direct evidence on the composition of the early atmosphere. Sediments and precipitates, because they are products of climate-sensitive processes, may provide a more direct indication of past climates. Various kinds of sediments are probably accessible. Included are alluvium on outwash plains of large floods, lake deposits

at the ends of outflow channels, fluvial terraces and bars, layered canyon deposits, and sediments in lakes fed by valley networks. Precipitates might include carbonates and other salts such as sulfates and nitrates. Of all these possibilities ancient lake beds are probably the most attractive. They will reveal information on chemical and physical conditions within the lake, the nature of contemporary weathering, the episodicity and carrying capacity of the feeder streams, the composition of contemporary volatiles, and so forth. Any ancient lake deposits are likely to be covered with younger deposits but samples should be available around impact craters. Impact craters are useful also in that they probably excavate materials from a variety of depths. For an early mission, not knowing the exact position of the samples in a section is less important than acquiring variety. Lake deposits from outflow channels are also of interest for climate studies. Some may contain thick ice deposits that formed shortly after the flood event. Other types of sediments such as fluvial terraces and bars may be better studied by rover missions than sample return missions

because much of the interest is in macrostructures such as cross-bedding rather than in the characteristics of small samples.

The need for mobility at the sample sites deserves emphasis. At any landing site we need to be able to view the scene and sample the diversity of the site. At a lake site, for example, we will need to go to the crater and sample material excavated by the crater. The mobility needs will depend in part on landing accuracy. The size and number of samples needed cannot be specified with assurance, but multiple samples, each weighing on the order of at least 100 g, are likely to be needed. If rock chips are present at the site, a rake sample would be useful.

In conclusion, the prime sample sites for climate studies are ancient lake beds and other ancient highland rocks. Simple atmosphere and regolith samples are also needed. A variety of small rock samples should be collected at each site, which probably implies having a rover.

Viewgraphs presented at meeting—

Geological Evidence for Climate Change

Erosion rates

Channels and valleys

Glaciation

Lakes and oceans

Weathered material

Polar deposits

Erosion Rates

Evidence for major changes in crater obliteration rates at end of Noachian unambiguous

Noachian craters several tens of kilometers across in all stages of preservation from well-preserved to barely visible depressions

Difficult to estimate erosion rates because cratering rates unknown

Best guess 10 mm yr⁻¹

Terrestrial rates mostly 10–1000 mm yr⁻¹

Average post-Noachian erosion rates three orders of magnitude lower

- ❖ Survival of craters at VL-1 site, 10⁻² mm yr⁻¹ (Arvidson et al., 1979); basal Hesperian crater populations, 2 × 10⁻² yr⁻¹ (Carr, 1992)
- ❖ Preservation of ejecta details on basal Hesperian craters, but not on Noachian (Craddock and Maxwell, 1993)
- ❖ Exceptions are seemingly wind-deposited and eroded deposits such as the Medusae Fossae Formation

Cause of change in obliteration rates unknown but climate change most probable

- ❖ Supported by high rates of valley formation at end of Noachian
- ❖ Water must have been widely distributed at end of Noachian, occurring at elevations as high as 4 km (sources of channels and valleys); implies active hydrologic cycle to maintain water at high elevations

Valley Networks

Dominant view, based mainly on planimetric shape, is that valleys are close analogs to terrestrial river valleys (i.e., formed by slow erosion of running water)

Main issues have been

- ❖ role of surface runoff (precipitation) vs. groundwater sapping
- ❖ whether warm climates are necessary for their formation

Valley network ages

- ❖ of 827 networks mapped 763 cut only Noachian
 - ◆ these networks could be younger than Noachian, but
 - ◆ many are transected by Hesperian intercrater plains so they truly are Noachian

- ◆ 34 networks cut Hesperian or older units
 - ◆ tributaries to canyons
 - ◆ steep slopes along plains/upland boundary
- ◆ 34 networks cut Amazonian
 - ◆ Almost all on volcanos
- ❖ Drainage densities
 - ◆ Drainage densities in Noachian uplands low, $0.001\text{--}01\text{ km}^{-1}$ compared with typically $2\text{--}30\text{ km}^{-1}$ for Earth (but may be scale problem)
 - ◆ Drainage densities on Amazonian volcanoes high, $0.3\text{--}1.5\text{ km}^{-1}$ (Gulick and Baker, 1990), but other Amazonian surfaces undissected.

Climatic Implications of Valley Networks

If valley networks are close analogs to most terrestrial river valleys (i.e., formed by slow erosion of running water), then warm climate conditions are almost certainly required whether fed by precipitation or groundwater

Modest sized streams (2–3 m deep) would rapidly freeze under present climate, although larger streams (floods >10 m deep) could probably survive and travel the >200 km needed to cut some networks

Precipitation needed either to

- ❖ feed streams directly, or
- ❖ recharge groundwater system—vs. larger amounts of water needed to cut by slow erosion (water/eroded volume >1000/1, Gulick and Baker, 1993), several kilometers over drainage basin (Goldspiel and Squyres, 1991)

So, warmer conditions required if formed by slow water erosion

Valleys may not be close analogs to terrestrial river valleys

River channels rare within valleys

Almost all upland valleys have rectangular x-section from source to mouth

Upland valleys do not divide upstream into ever smaller valleys (almost all wider than 2 km)

Some valleys have central ridges and levee-like peripheral ridges so floors not flood plains

Some valleys, particularly young ones, appear to be caused by local rather than global conditions
Amazonian volcanos (hydrothermally fed streams eroding ash deposits?)

Steep canyon walls, cliffs on plains/upland boundary, crater walls

So what is the origin of the valleys?

We don't know

Variety of processes could have contributed

Slow erosion of precipitation-fed streams

Slow erosion of groundwater-fed streams

Slow erosion of streams fed by hydrothermal springs

Small episodic floods of groundwater

Water- or ice-abetted mass-wasting

Combination of all of the above, the mix varying with time and place

Thus, valleys present a suggestive but not compelling case for warm climates late in Mars' history

Glaciation

Glaciation invoked by Kargel and Strom (1992) to explain a number of different features, mainly in Hellas, Argyre and the northern plains

If features are glacial, then precipitation and warm climates needed late in Mars' history

But all features listed have other possible interpretations

Lakes and Oceans

Large bodies of water must have formed at the ends of the large outflow channels

Issues are sizes and climatic effects

Baker et al. (1991) suggested oceans ranging in volume from $1-6 \times 10^7 \text{ km}^3$ and covering areas of $1.4-3.8 \times 10^7 \text{ km}^2$ formed episodically throughout martian history temporarily changing global climates

Parker et al. (1989, 1993) identified "shorelines" around areas of 2.7×10^7 and $4.6 \times 10^7 \text{ km}^2$

Others (e.g., Carr, 1990) suggest that lakes containing 10^5-10^6 km^3 (size of individual floods) froze in place and had a negligible effect on climate

Loose Air-Deposited Surface Materials

Observed as drifts at the two Viking landing sites

Several areas at low latitude where an etched deposits lie unconformably on more resistant "bedrock" (e.g., Medusae Fossae Formation and area northwest of Isidis).

Drifts at VL sites appear to be products of weathering; are other deposits of same materials?

Evidence of high rates of erosion during Noachian. Where did the erosion/weathering products go to? Are these deposits the missing material?

Duricrust at VL sites indicates movement of soluble salts in soil profile. Could the movement occur under present climates or do they record other climatic conditions? Formation of the duricrust at VL-1 occurred after (possibly well after) deposition of the local Hesperian bedrock, so could indicate late climate changes

Polar Deposits

Polar deposits are stacks of sediments a few kilometers thick that extend approximately 10° of latitude from each pole. They have horizontal layering and unconformities visible down to the limiting resolution of the available photography ($\sim 50 \text{ m}$). The average age of the surface in the south is 10^8 yr . The upper surface in the north appears to be younger.

Layering has been attributed to modulation of deposition of dust and volatiles by variations in orbital and rotational motions.

However, connection between layering and orbital motions is not established, and the age of the surface in the south indicates that 50-m layering is due to accumulation over 10^7 -yr timescales, not the 10^5 -yr obliquity timescales (Plaut et al., 1988). They could be mainly a record of stochastic events such as floods and volcanic eruptions and not a record of changes induced by planetary motions.

Polar terrains may provide a semicontinuous record of erosion/sedimentation, condensation/sublimation for as long as 1 G.y. so they may provide a fairly complete climatic record for late Mars history.

Conclusions

Evidence for warm climates during Noachian strong (high erosion rates, high rates of valley formation, water widely distributed irrespective of elevation)

If warm climates in Noachian then rocks should preserve a record in rock types (gravels, evaporites, etc.), macrostructures (bedding, disconformities, etc.), microstructures (grain size, sorting, etc.), mineralogy, and so forth

Evidence from warm climates after the end of the Noachian less compelling but still strongly suggestive

Need to better understand mode of formation of valley networks

Need to better understand mode of formation of "glacial" features

Need to determine the depositional environments (lacustrine?) at the ends of both valley networks and outflow channels

Need to look at the timing and nature of weathering and soil profile development

Need to look at polar record

Regolith and Climate

Issues

Source of loose material

- ❖ Weathering products of primary rocks
- ❖ Primary volcanic component—pyroclastics, water/ice interactions
- ❖ Meteorite component

Modelage of constituent materials

- ❖ Weathering mostly in Noachian?
- ❖ Continuous supply throughout Mars history?

Physical-chemical conditions under which weathering occurred

- ❖ Former warm/wet conditions?
- ❖ Photostimulated weathering under current climate?

Erosion/depositional history

- ❖ Deposits stable—record long history of postdepositional alteration?
- ❖ Deposits repeatedly eroded and deposited?

Alteration history

- ❖ How and when did duricrust form?
- ❖ Climatic conditions under which duricrust formed?
- ❖ Multiple soil profiles recording multiple climatic episodes?

Efficacy as a source/sink for volatiles?

Types of samples needed

Probably >60% of the issues can be addressed with 1–2 scoops (a few hundred milligrams each) that included both indurated (duricrust) and nonindurated components.

If first sample site turns out to be identical to Viking this would indicate that loose air-deposited material is the same everywhere, so there would be little to gain getting similar samples at multiple locations

Preferable to get 1-m core through soil profile

Types of measurements to be made

Chemistry/mineralogy

- ❖ conditions at time of weathering
- ❖ meteorite/volcanic contributions
- ❖ chemical stability

Isotopics (O, D/H, C, S, etc.)

- ❖ values at time of weathering

Modelages (K/A?, Rb/Sr?)

Exposure ages—short-lived cosmic-ray-induced activity

Adsorbed gases

Prior knowledge needed to acquire sample

Probably available at most sites

Massive Air Fall Deposits and Climate (Medusae Fossae Formation, various etched deposits)

Issues

Same as for regolith, but these deposits are probably more stable so may provide a significantly longer record of erosion and deposition, with multiple soil profiles. May be analogous to polar layered deposits (or identical—Schultz and Lutz, 1988)

Are these deposits of weathered material or of some other origin (polar, pyroclastics, etc.)?

Types of samples needed

Scoops

Sample from present surface down to depth of 1 m

Samples through fossil soil horizons

Types of measurement to be made

Same as for regolith

Prior knowledge needed

Need to close visual observations

- ❖ Are these horizontally layered deposits, if so on what scale?
- ❖ Are there weathering horizons between layers?

Sediments and Climate

May be of several types

Alluvium on outwash plains of outflow channels

“Lake deposits” from outflow channels

Alluvial terraces, bars, etc., within outflow channels

Fans at mouths of valley networks

Deposits on floors of valley networks

Deposits in lakes fed by valley networks

Layered canyon deposits

Various colluvial deposits (debris aprons, fretted valley floors, etc.)

Issues to be addressed

Hydraulic conditions during sediment transport and deposition (climatic implications)

Episodicity of deposition (climatic variations)

State of disaggregation/preservation of source rocks

Conditions in lakes

Isotopics of contemporary waters (outgassing, loss to space, etc.)

Chemistry of waters (vs. saline?)

Amounts and types of samples

Sample return may not be the best way to address most of the issues listed above

Need information at the centimeters to meters scale (layering, cross-cutting patterns, size fractionation, weathering horizons between beds, etc.); subcentimeter texture/chemistry derived from samples probably less important, at least for alluvial and colluvial sediments

Need careful selection of sample site (highly fractionated rock, e.g., sandstone may tell little of primary source rocks or depositional processes)

Implies capable rover to document macrostructures and choose site for returned samples

Measurements to be made on samples

Petrologic examination (including SEM) and supporting context information will provide most clues about the mode of deposition, particularly for alluvial and colluvial deposits

Detailed mineralogy and petrology will also provide information on state of weathering of source rocks, and any post-depositional alteration and cementation

Chemistry (including organics) and isotopics of lake sediments will provide information on conditions within the lakes (eH, pH, salinity, etc.)

Chemical Precipitates

Chemically precipitated rocks have yet to be identified

Evaporites?

Carbonates (where are all the carbonates?)

Hydrothermally deposited minerals

Issues that might be addressed

Conditions under which evaporation occurred (warm climates?)

Conditions under which alteration occurred to produce solutes

❖ Eruption of saline groundwater?

❖ Surface alteration during warmer climates

Isotopic composition of contemporary H, O, C, N, S, etc.

Volatile inventories

Types of samples

Random small sample would provide useful information, particularly on isotopics

Vertical section through evaporite useful for depositional sequence; depth of section depends on scale of laminations (salt succession gives water chemistry, perhaps temperature)

Prior to sample return mission should determine:

If evaporite/carbonate/hydrothermal deposits exist and if so, where (remote sensing)

Gross character of deposits (vertical bedding, lateral homogeneity, etc.)

Polar Deposits

Issues that could be addressed

The polar deposits appear to represent a fairly continuous record of the last few hundred million years (at least in the south)

Probably the best place to find record of climatic events in second half of Mars history

Particularly suitable for looking at how isotopics evolved with time

Can assess size of the polar volatile reservoir and whether high obliquities could cause or have caused significant climate changes

Types of samples needed

Ideally should take samples through as thick a section as possible

Failing that, sample at top of section, then 1–2 km deeper (either two landings or move down-section)

Failing that, get sample at base of section (old) rather than top (recent)

Individual samples need not be large (few hundred milligrams sufficient) but should be preserved at least at temperatures well below freezing (-20°C ?)

Measurements to be made

- ❖ Layer to layer variations in chemistry, mineralogy, isotopics, petrography
- ❖ Nature of interface between layers (evidence of erosion/weathering)
- ❖ Vertical variations in cosmogenic nuclei (^{10}Be , ^{26}Al) to get deposition/erosion rates

Prior information needed

May have enough information now to choose decent sites, but better imaging of southern terrains desirable

Other Materials

Water-ice

May be accessible at shallow depths at latitudes >40

Isotopics may give indication of whether there was exchange with atmosphere

Is this worth trying for?

Dune materials

Although dune formation is probably a climate-sensitive process, I doubt these deserve much attention

Robert M. Haberle, NASA Ames Research Center—

The Status of Mars Climate Change Modeling

M. Carr and B. Jakosky have reviewed the evidence that the climate of Mars has changed throughout its history. My talk at the workshop reviews where we stand in terms of modeling these climate changes. For convenience, three distinct types of climate regimes are considered: very early in the planet's history (>3.5 Ga), when warm wet conditions are thought to have prevailed; the bulk of the planet's history (3.5–1 Ga), during which episodic ocean formation has been suggested; and relatively recently in the planet's history (<1 Ga), when orbitally induced climate change is thought to have occurred.

Early Mars Greenhouse Models: The valley networks and highly eroded landforms of the late Noachian period imply that liquid water was stable at that time. The most plausible way to produce such conditions is to invoke the greenhouse effect of a more massive $\text{CO}_2/\text{H}_2\text{O}$ atmosphere than the one we see today. During the 1970s and 80s one-two-dimensional models were developed that showed that global mean temperatures could reach 273 K in the presence of a less luminous Sun if the atmosphere contained between 1–5 bar of CO_2 , an amount consistent with estimates of the planets' volatile inventory. The lifetime of such an atmosphere against weathering has been estimated to be 10–500 m.y. and could be sustained for comparable times by "hot spot" volcanism or impact cratering. However, these early greenhouse models are flawed because they do not account for atmospheric CO_2 condensation, which can greatly retard the greenhouse effect. Furthermore, atmospheric evolution models are unable to arrive at current conditions from a massive early $\text{CO}_2/\text{H}_2\text{O}$ atmosphere. At the present time, there is no resolution of this dilemma. The geological evidence suggests warm and wet conditions, but the climate models are unable to show how this can occur. Some possible solutions include a brighter early Sun, the presence of reduced greenhouse gases, and

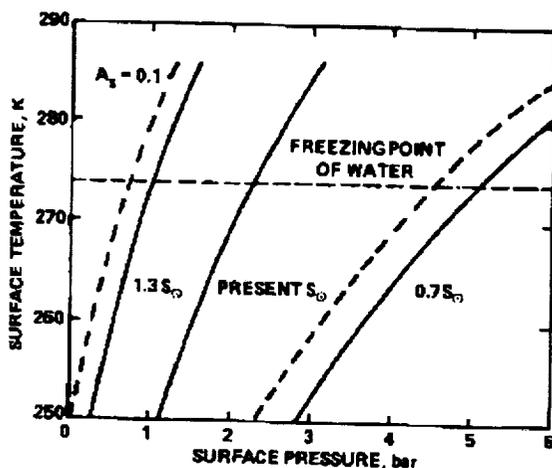


Fig. 1. Global mean surface temperature as a function of surface pressure for several values of the solar constant. Solid lines assume an albedo of 0.25; dashed lines an albedo of 0.10. From Pollack et al. (*Icarus*, 71, 1987).

a scattering greenhouse effect. But these all have difficulties. It is also possible that the models are missing some important physics, or that networks and eroded landforms actually formed in cooler environments than have been suggested. But without more work and/or data, we cannot determine which of these possible solutions is correct.

Episodic Ocean Formation: Baker et al. (1991) have suggested that a variety of surface features (young networks, eskers, sedimentary deposits, shorelines) could be explained by episodic ocean formation throughout Mars' history. These oceans would form in days to years as the result of flooding associated with volcanic activity in the Tharsis region. The oceans are expected to contain large amounts of dissolved CO_2 , which would come out of solution and go into the atmosphere. The released CO_2 and H_2O would increase the greenhouse effect which would then force even more CO_2 into the atmosphere from the regolith and polar cap reservoirs. Baker et al. estimate that as much as 4 bar could be added to the atmosphere by this mechanism. Thus, after ocean formation, the climate would warm and a hydrologic cycle would develop. Weathering would draw down atmospheric CO_2 and the ocean would eventually be returned to the groundwater system. The processes associated with this scenario are poorly understood, as no modeling has appeared in the literature. However, Gulick et al. have recently submitted a paper to *Icarus* in which they address the duration and thermal environment of an ocean-induced climate event. They find that a 1–2-bar pulse of CO_2 occurring anytime

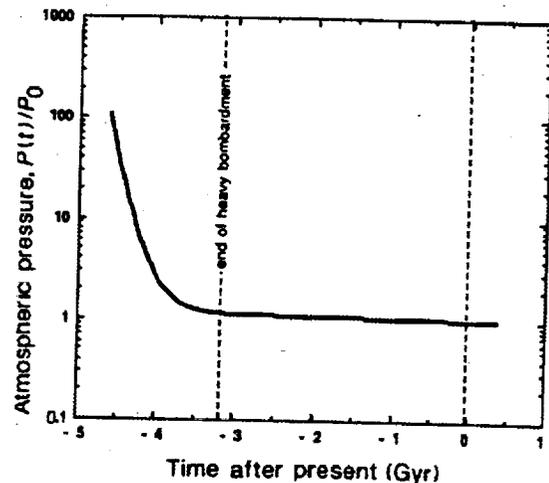


Fig. 2. Evolution of the atmospheric pressure $P(t)$ on Mars relative to its present value P_0 . This figure is constructed using the following equation, assuming $t^* = 63.1$ G.y., $B = 2300$, and $\lambda = 4.53$ G.y. $^{-1}$. It shows the rapid decline in Mars' atmospheric pressure throughout the era of late heavy bombardment.

$$\frac{M_{\text{atm}}(t)}{M_0} = \frac{P(t)}{P_0} = \left(1 - \frac{t}{t^*} - \frac{B e^{-4.6\lambda t}}{\lambda t^*} [1 - e^{-\lambda t}] \right)^{1/b}$$

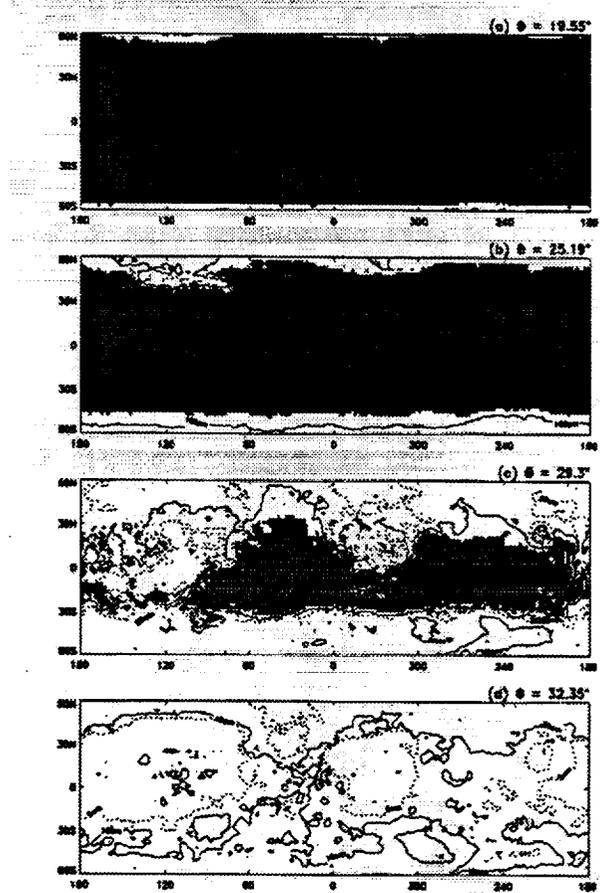
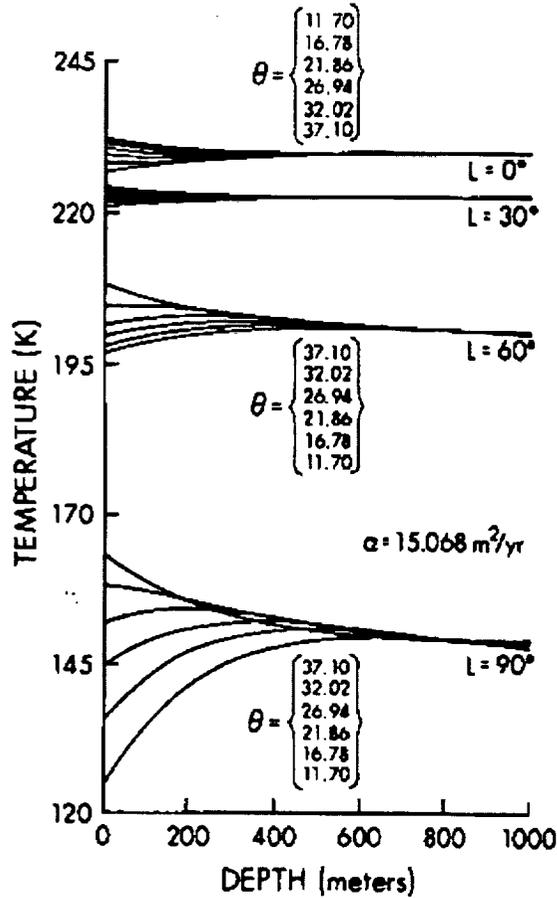
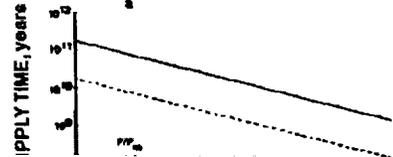
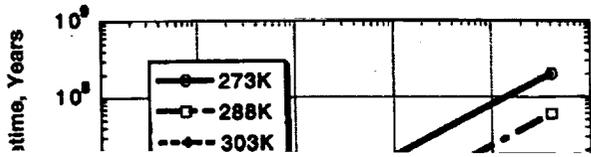
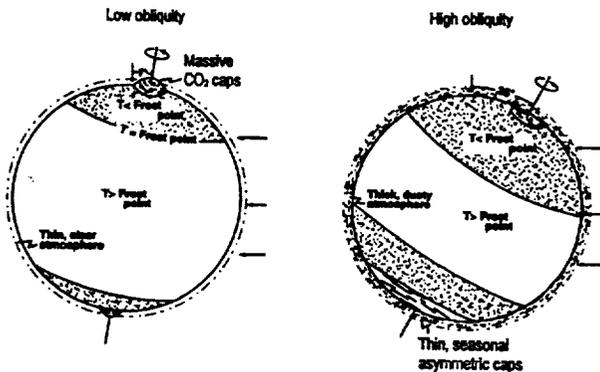
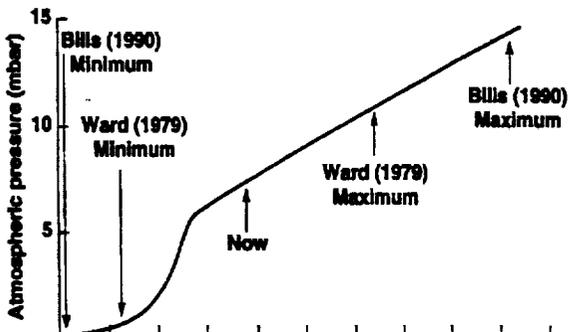


Fig. 13. Models of the stability of ground ice.

Fig. 11. Temperature in the regolith for four latitudes L during a period of increasing obliquity. Thermal diffusivity is assumed to be $15 \text{ m}^2/\text{yr}^{-1}$, and internal heat flow is neglected (figure from Fanale et al., 1982a).



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Early Mars Greenhouse Models: The valley networks and highly eroded landforms of the late Noachian period imply that liquid water was stable at that time. The most plausible way to produce such conditions is to invoke the greenhouse effect of a more massive $\text{CO}_2/\text{H}_2\text{O}$ atmosphere than the one we see today. During the 1970s and 80s one-two-dimensional models were developed that showed that global mean temperatures could reach 273 K in the presence of a less luminous Sun if the atmosphere contained between 1–5 bar of CO_2 , an amount consistent with estimates of the planets' volatile inventory. The lifetime of such an atmosphere against weathering has been estimated to be 10–500 m.y. and could be sustained for comparable times by "hot spot" volcanism or impact cratering. However, these early greenhouse models are flawed because they do not account for atmospheric CO_2 condensation, which can greatly retard the greenhouse effect. Furthermore, atmospheric evolution models are unable to arrive at current conditions from a massive early $\text{CO}_2/\text{H}_2\text{O}$ atmosphere. At the present time, there is no resolution of this dilemma. The geological evidence suggests warm and wet conditions, but the climate models are unable to show how this can occur. Some possible solutions include a brighter early Sun, the presence of reduced greenhouse gases, and

a scattering greenhouse effect. But these all have difficulties. It is also possible that the models are missing some important physics, or that networks and eroded landforms actually formed in cooler environments than have been suggested. But without more work and/or data, we cannot determine which of these possible solutions is correct.

Episodic Ocean Formation: Baker et al. (1991) have suggested that a variety of surface features (young networks, eskers, sedimentary deposits, shorelines) could be explained by episodic ocean formation throughout Mars' history. These oceans would form in days to years as the result of flooding associated with volcanic activity in the Tharsis region. The oceans are expected to contain large amounts of dissolved CO_2 , which would come out of solution and go into the atmosphere. The released CO_2 and H_2O would increase the greenhouse effect which would then force even more CO_2 into the atmosphere from the regolith and polar cap reservoirs. Baker et al. estimate that as much as 4 bar could be added to the atmosphere by this mechanism. Thus, after ocean formation, the climate would warm and a hydrologic cycle would develop. Weathering would draw down atmospheric CO_2 and the ocean would eventually be returned to the groundwater system. The processes associated with this scenario are poorly understood, as no modeling has appeared in the literature. However, Gulick et al. have recently submitted a paper to *Icarus* in which they address the duration and thermal environment of an ocean-induced climate event. They find that a 1–2-bar pulse of CO_2 occurring anytime

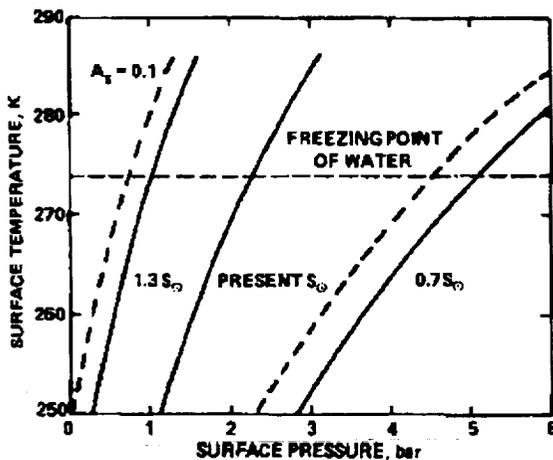


Fig. 1. Global mean surface temperature as a function of surface pressure for several values of the solar constant. Solid lines assume an albedo of 0.25; dashed lines an albedo of 0.10. From Pollack et al. (*Icarus*, 71, 1987).

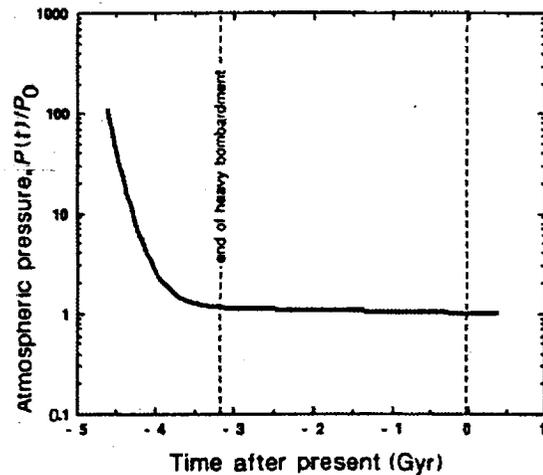


Fig. 2. Evolution of the atmospheric pressure $P(t)$ on Mars relative to its present value P_0 . This figure is constructed using the following equation, assuming $t^* = 63.1$ G.y., $B = 2300$, and $\lambda = 4.53$ G.y. $^{-1}$. It shows the rapid decline in Mars' atmospheric pressure throughout the era of late heavy bombardment.

$$\frac{M_{\text{atm}}(t)}{M_0} = \frac{P(t)}{P_0} = \left(1 - \frac{t}{t^*} - \frac{B e^{-4.6\lambda t}}{\lambda t^*} [1 - e^{-\lambda t}] \right)^{1/b}$$

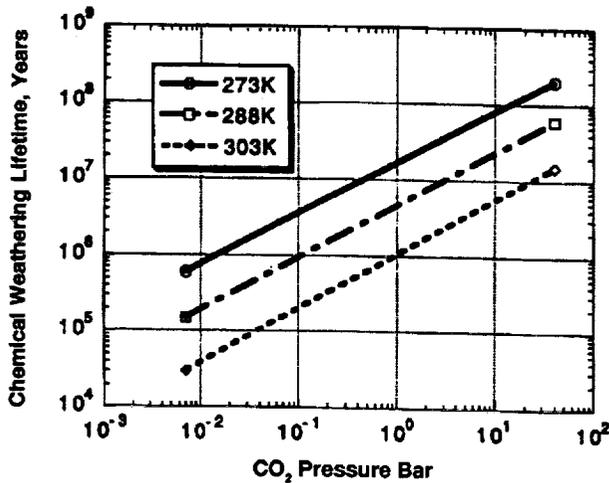


Fig. 3. Chemical weathering lifetime of a CO₂ atmosphere as a function of surface pressure for three different temperatures. Adapted from Pollack et al. (*Icarus*, 71, 1987).

during the past several billion years is capable of raising global mean temperatures to 240–250 K for tens to hundreds of millions of years. Such an increase could drive a limited hydrological cycle and possibly explain the younger valleys and putative glacial features. However, many details remain, most notably the possibility for multiple ocean-forming events since the first event would convert a large amount of CO₂ into carbonates.

Quasi-Periodic Climate Change: State-of-the-art orbital models predict significant variations in the eccentricity, precession, and obliquity of Mars. These variations are predictable only for the past 10 m.y. Beyond that time, orbit parameters become chaotic. Obliquity variations have received the most attention because they are large (0°–60° over the planet's history) and they determine the latitudinal distribution of solar insolation and hence the ultimate distribution of CO₂ and H₂O in the regolith-atmosphere-cap system.

As the obliquity increases the following are expected to occur: Polar regions warm and equatorial regions cool. Any CO₂ in the polar regolith would be driven into the atmosphere and surface pressures would rise. Models indicate that the increase in surface pressure would be less than 25 mbar - if there is not a large reservoir of CO₂ as ice or clathrate buried in the polar regions. If there is, an increase of 200 mbar or so is plausible, but even this amount is not enough for significant greenhouse warming. Ice could become globally stable at the surface, whereas it is only stable at the poles today. Dust storms would occur more frequently due to the increase in atmospheric mass and the intensity of the solstice circulation.

As the obliquity decreases the following are expected to occur: Polar regions cool, CO₂ returns to the polar regolith, and permanent polar caps eventually form. At this point the planet transitions from a regolith-buffered system to a cap-buffered system. Much of the regolith CO₂ would be transferred to the caps, which could become quite large. Surface pressures could fall to 0.5 mbar or less, making CO₂ no longer the main atmospheric constituent. Dust storms would cease and the caps would cold trap water desorbing from the regolith.

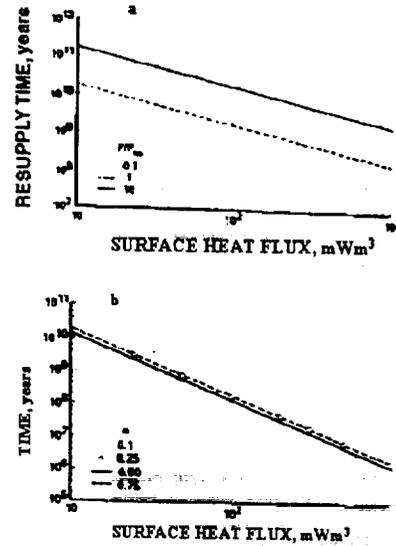


Fig. 4. Timescale for resupplying the atmosphere with CO₂ as a function of the surface heat flux from the interior. Results are shown for (a) outgassing of juvenile CO₂ from the planet's interior (the three curves correspond to alternative choices for the ratio of CO₂ in the atmosphere to that in the interior) and (b) a recycling mechanism, for which carbonate rocks formed by weathering are thermally decomposed after being buried by lava to a sufficient depth. The curves differ in the choice of the fraction of the heat flux carried by thermal conduction, a.

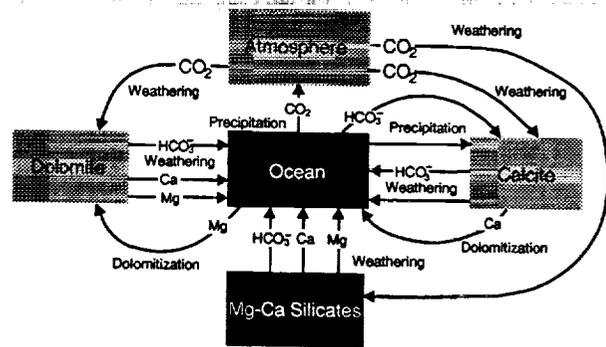


Fig. 5a. A schematic diagram.

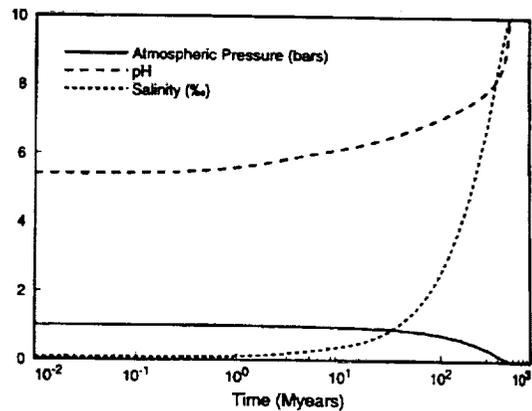


Fig. 5b. Variation of pressure.

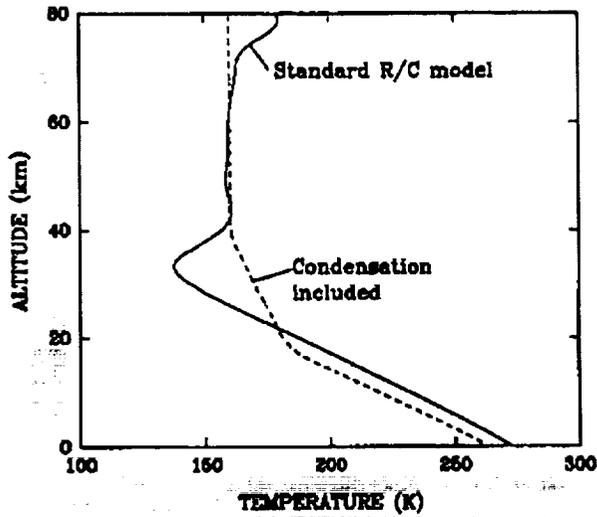


Fig. 6a. Vertical temperature profiles.

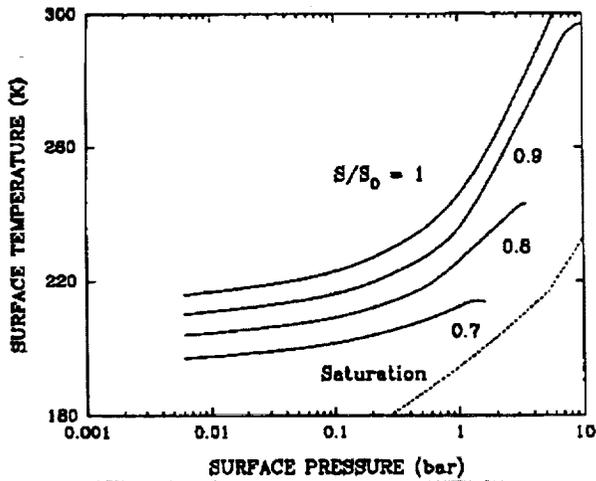


Fig. 6b. Surface temperature vs. surface pressure.

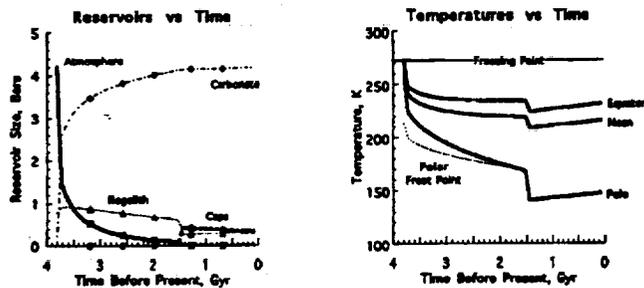


Fig. 7. Left: Evolution of various CO₂ reservoirs as a function of time. Right: Surface temperatures as a function of time.

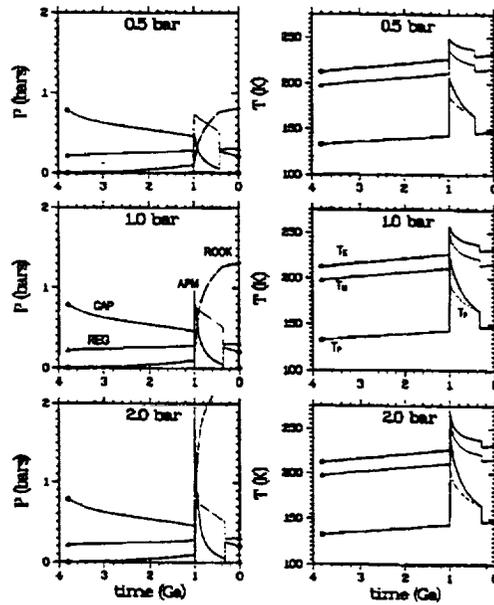


Fig. 8. Same as Fig. 7 but with the introduction of a 0.5 (top), 1.0 (middle), and 2.0 (bottom) bar "pulse" of CO₂ at one billion years ago. These pulses are assumed to result from the formation of an ocean due to volcanic activity as described Baker et al. Figure from Gulick et al. (*Icarus*, submitted 1996).

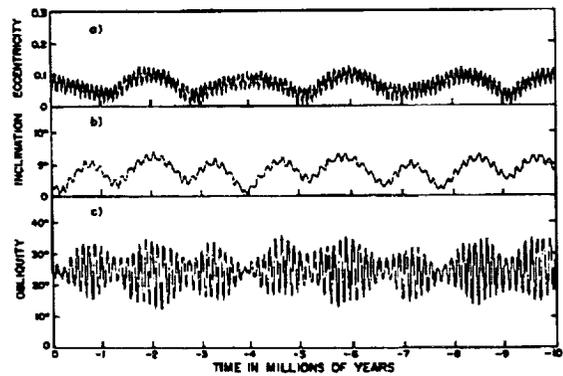


Fig. 9. Same as Fig. 5.

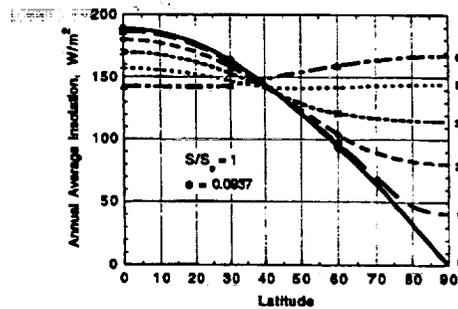


Fig. 10. Annual average insolation at the top of the atmosphere for several different obliquities as a function of latitude. Calculations assume present day solar luminosity and Mars eccentricity.

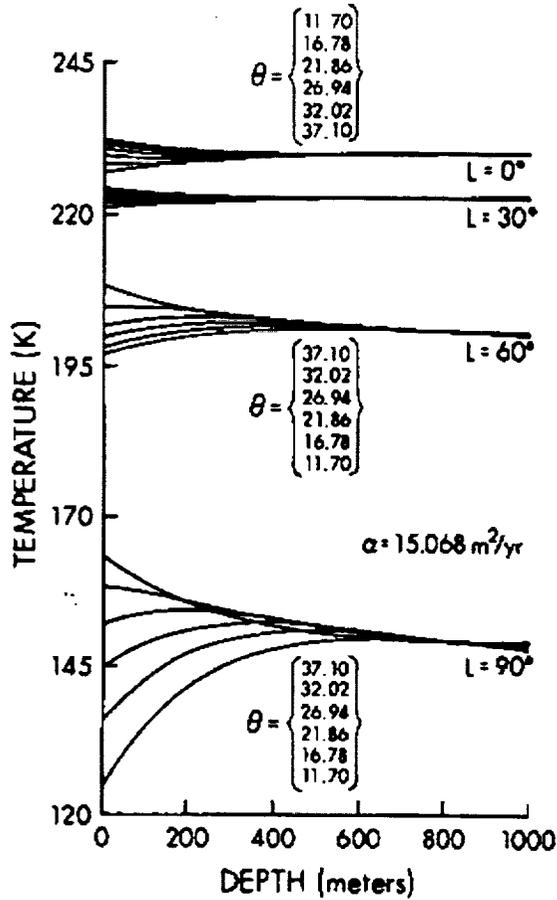


Fig. 11. Temperature in the regolith for four latitudes L during a period of increasing obliquity. Thermal diffusivity is assumed to be $15 \text{ m}^2/\text{yr}^{-1}$, and internal heat flow is neglected (figure from Fanale et al., 1982a).

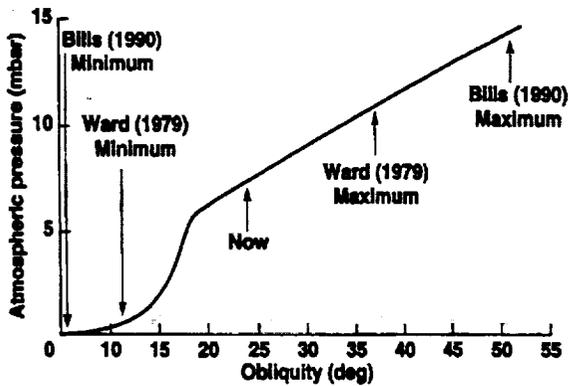


Fig. 12. Atmospheric pressure as a function of obliquity as predicted by the model of Fanale et al. (1982).

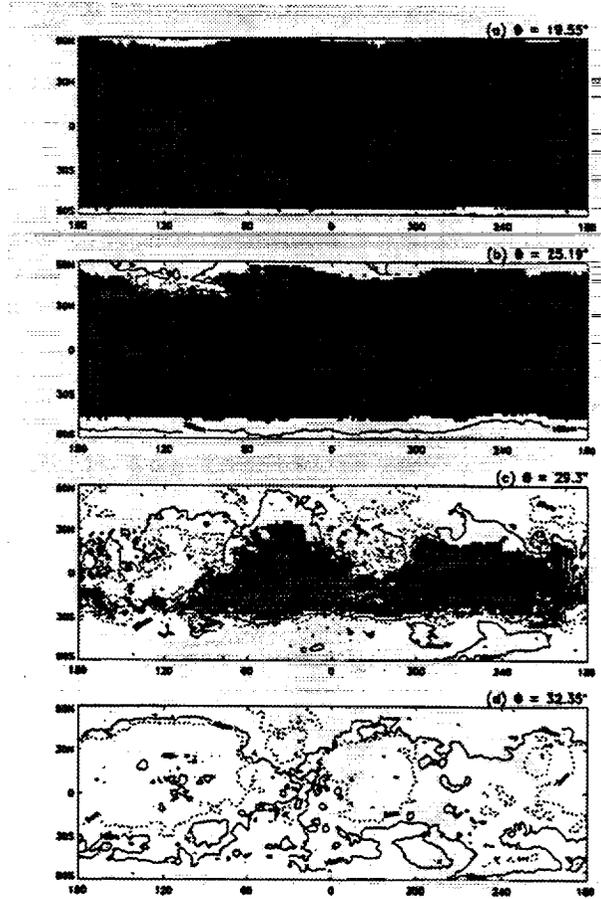


Fig. 13. Models of the stability of ground ice.

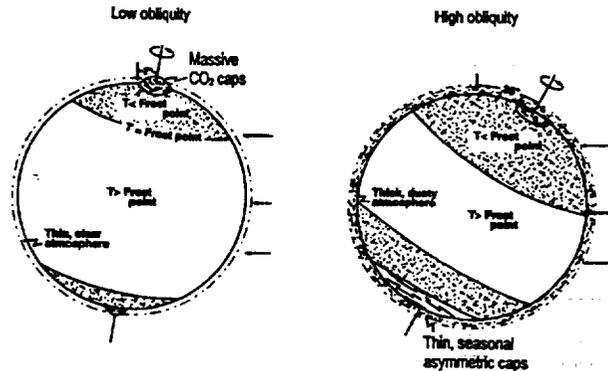


Fig. 14. Cartoon of the conditions on Mars at the extremes of obliquity. At low obliquity (left) permanent caps form, atmospheric pressure drops, dust storms cease, and water is cold trapped at the poles. At high obliquity (right) the caps vaporize, CO_2 desorbs from the polar regolith, surface pressure rises, dust storms occur frequently, and ground ice can be stable to very low latitudes. From Kieffer and Zent (Kieffer et al., eds., Univ. Arizona Press).

Viewgraphs presented at meeting—

Early Mars Greenhouse Models

Mariner 9 fluvial features → greenhouse effect

Faint young Sun paradox:

Solar luminosity 25% less 3.8 Ga

Yet sedimentary rocks found on Earth at 3.8 Ga

NH₃ was greenhouse gas (Sagan and Mullen, 1972)

But has short photochemical lifetime (Kuhn and Atrea, 1979)

CO₂/H₂O atmosphere best candidate

Larger amounts expected to be degassed early on

CO₂ is photochemically stable

One- and two-dimensional models of 1970s and 1980s required 1–5 bar of CO₂ for T_m = 273 K

Consistent with estimates of volatile inventory

But maintenance an issue (impact erosion, carbonate formation)

Volcanic burial (Pollack et al., 1987) and/or impact recycling (Carr, 1989) could recharge the atmosphere

Atmosphere CO₂ condensation reduces greenhouse (Kasting, 1991)

T_m < 214 K at 3.8 Ga

Difficult to arrive at current conditions from warm wet early Mars (Haberle et al., 1994)

Some Possible Solutions to the Early Mars Dilemma

Early Sun was brighter than stellar models predict

10% mass loss could explain ⁷Li depletion (Boothroyd, 1991)

But Sun would be too bright (Earth's oceans would evaporate)

2% mass loss is optimum (Kasting, 1991)

CO₂/H₂O greenhouse augmented by reducing gases (e.g., CH₄, NH₃, SO₂)

Short photochemical lifetimes

Source needs to be identified

CO₂ clouds might have a scattering greenhouse effect

Radiative properties not known

Could be mixed with dust and water

The climate models are flawed

Clouds, multidimensional calculations are needed

Valley formation and early high erosion rates occurred in cooler environmental conditions than presumed

Ocean-Induced Climate Change

Young networks, glacial features, sedimentary deposits, and possible shorelines → episodic oceans (Baker et al., 1991)

Oceans form in days to years by volcanically driven flooding

CO₂ released from groundwater warms the climate, causing more CO₂ release from regolith, caps, and clathrates

Up to 4 bar of CO₂ could be released (Baker et al. estimate)

Degree of warming depends on timing and amount released

Stability of ocean-induced climate change (Gulick et al., 1996)

1–2 bar “pulses” during past several billion years raise T_m above 240–250 K for tens to hundreds of millions of years

Limited hydrological cycle possible

Could explain Amazonian erosion and valley formation

Issues: processes poorly understood

Source of CO₂

Cloud radiative feedbacks

Possibility of multiple events (CO₂ → carbonates)

Quasiperiodic Climate Change

Mars orbital parameters vary significantly and are chaotic on timescales > 10⁷ years

Eccentricity → seasonal asymmetry

Precession → longitude of perihelion

Obliquity → latitudinal distribution of insolation

Changes in obliquity affect distribution of CO₂ and H₂O in regolith, atmosphere, and caps

For regolith/atm system mass surface pressure <25 mbar at high obliquity (Fanale et al., 1982), but 15 mbar more likely

Polar regions could have 200–800 mbar CO₂ (Jakosky et al., 1995), but >200 mbar unlikely (Mellon, 1996; Haberle and Tyler, 1996)

Water ice globally stable at high obliquity (Mellon and Jakosky, 1995), but where does polar ice go?

Dust storm frequency increased with obliquity but need not be associated with increasing surface pressure (Haberle, 1996)

Layered deposits could be buried ice sheets (Toon et al., 1980)

Consistent with estimated density (Malin, 1986)

Inconsistent with estimated age (Platt, 1988)

Issues Regarding Quasiperiodic Climate Change

Quasiperiodic climate change must occur, but nature of change is uncertain

Need better information on:

- Composition, depth, distribution, and pore size of regolith

- Composition and stratigraphy of polar layer terrains

- Presence of buried polar CO₂ ice deposits

- Distribution of ground ice

Need better modeling of:

- Effect of dust on cap albedo

- Dust storm generation

- Atmospheric water transport

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Sample Return Needs

Bruce M. Jakosky, University of Colorado—

Science Goals for a Returned Sample of the Martian Atmosphere

Isotope ratios in present-day martian atmosphere (C, H, N, O, noble gases)

Purpose: To use isotopic measurements to constrain the processes by which the atmosphere has evolved. For the noble gases, relevant processes include early hydrodynamic escape and sputtering by solar-wind pickup ions. For C, H, N, and O, these same processes act, and processes related to exchange with nonatmospheric reservoirs can act.

Measurements of interest:

- ❖ $^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$ in CO_2
- ❖ $^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$ in H_2O
- ❖ $^{13}\text{C}/^{12}\text{C}$ in CO_2
- ❖ D/H in H_2O
- ❖ $^{40}\text{Ar}/^{38}\text{Ar}/^{36}\text{Ar}$
- ❖ $^{22}\text{Ne}/^{20}\text{Ne}$
- ❖ $^{78/80/82/83/84/86}\text{Kr}$
- ❖ $^{124/126/128/129/130/131/132/134/136}\text{Xe}$

Issues:

- ❖ How much sample is required for this analysis?

^{14}C abundance in atmosphere

Purpose: To constrain regolith-atmosphere mixing of CO_2 by looking at the size of the reservoir that is able to exchange on the timescale of the ^{14}C half-life. Although this is an isotopic measurement, the technique is different from that of the other noble gases, so it is listed separately.

Measurement of interest:

- ❖ $^{14}\text{C}/^{12}\text{C}$ in CO_2

Issues:

- ❖ How much sample is required for this analysis?

Properties of airborne dust

Purpose: To constrain the physical properties and composition of airborne dust in order to understand its radiative effects on climate.

Measurement of interest:

- ❖ Dust abundance in sample
- ❖ Grain size distribution
- ❖ Particle shapes
- ❖ Particle composition

Issues:

- ❖ Small number of dust grains available in a sample of atmosphere (for an atmospheric column dust opacity of one, there are only on the order of 100 dust grains per cubic centimeter of gas)
- ❖ Can the number of dust grains that are returned be increased by filtering the gas?

Detection of stable minor species

Purpose: To measure the abundance of atmospheric minor gases that are stable against chemical reactions on the timescale of the mission. Species out of chemical equilibrium will tell us about possible biological activity. Helium will tell us about recent outgassing.

Measurement of interest:

- ❖ Mixing ratios of CH₄, NH₃, H₂S, He, for example

Issues:

- ❖ How much gas must be returned to provide a detection or a useful upper limit?

Detection of reactive minor species

Purpose: To measure the abundance of minor species that may react chemically with other species or with the walls of the container on the timescale of the mission. For this reason, it may not be feasible to measure them, or, if measurable, the results may not be interpretable.

Measurements of interest:

- ❖ Mixing ratios of CO, O₂, O₃, H₂O₂

What about water?

Purpose: To determine the mixing ratio of water in the atmosphere at the location and season of sampling.

Measurement:

- ❖ Water vapor mixing ratio

Issues:

- ❖ Water vapor can be more easily determined *in situ* at a variety of seasons
- ❖ There may be a trade-off between water vapor and sorbed water, so that the abundance may not be so useful
- ❖ Water is difficult to measure because of contamination and trapping issues

Polar ice

Purpose: To determine ice composition, isotope ratios, and dust abundance and composition in polar ice.

Measurement:

- ❖ All of the above in a returned sample of polar ice

Issues:

- ❖ Can an ice core be obtained?

Other Issues to Consider

There is obvious synergy of the isotope measurements with those obtained from other aspects of the returned samples. Comparison of isotope abundances in atmosphere with those in various components of the rocks and soil weathering products is of high value; especially relevant and useful would be any information on the time history of isotope ratios that could be obtained from weathering products.

The questions raised here may be addressed in part by measurements that may be obtained by earlier missions. Not all important species will be measured, however, so these results will still be of very high value.

Can any altitude information be obtained by collecting gas during the lander entry? There would be enough gas available since Viking, for example, was able to obtain vertical profiles of isotope ratios. Each altitude that is sampled would require a separate canister. The most useful information may be on the altitude of the homopause and the properties of dust at high altitudes.

Sample Issues and Requirements

Amount of sample required:

¹⁴C constraint may be most stringent

- ❖ 2×10^{-3} g CO₂ more than adequate
- ❖ Contained in 1-cm³ atmosphere sample at STP
- ❖ Equivalent to 20-cm cube sample container at Mars ambient

Sample would need to be divided among multiple labs (e.g., ¹⁴C, stable isotopes, noble gases)

- ❖ Large container? Compress gas for storage?

Polar ice sample: Minimum of several grams

Special preservation needs:

Gas: No requirements (except airtight container)

Dust: No extreme temperatures (e.g., 200 K < T < 320 K)

Ice: Temperatures substantially below melting and low enough to minimize sublimation (e.g., T < 200 K); sealed container

Prior knowledge or contextual information for samples:

None

Laurie Leshin, UCLA—

Sample Return and Climate: Igneous Rocks and Impact Breccias

The major outstanding issue in studies of martian climate is whether or not Mars was warmer and/or wetter in its earliest history [1], i.e., during the Noachian, the time period when most of the valley networks were formed [2]. In order to address the scientific questions associated with evolution from the early martian climate to that of today, we must proceed with two types of studies. First, it is critical to understand the distribution and composition (both molecular and isotopic) of the current martian volatile inventory. Specifically, detailed chemical and isotopic analysis of the current atmosphere (discussed at this workshop from the perspective of sample return by B. Jakosky and T. Owen) and mineralogical, petrological, and chemical characterization of young martian rocks (such as, but not limited to, most of the SNC meteorites), as well as mapping of the current distribution of groundwater/ice (not accomplished by sample return missions) will lead to an understanding of the current product of Mars' early climate/volatile evolution. Second, and even more critical, are studies of ancient (Noachian) rocks that preserve a record of this ancient martian climate. Ancient sediments are obviously an immensely interesting target for a sample return effort, but Noachian igneous rocks and impact breccias would also give important insights into the earliest volatile history of Mars, and they are the focus of this discussion.

In general, the minerals and glasses that comprise igneous rocks are unstable at the surface of a terrestrial planet. Given enough time and the proper physical and chemical conditions, this disequilibrium leads to formation of secondary alteration products that record information about the environment in which they were formed. By studying the products of the interaction of igneous rocks with their environment, it is possible to reconstruct the environmental conditions under which the alteration products formed. In addition, magmas that come into contact with volatile-rich regions upon emplacement (e.g., groundwater, oceans) have distinctive textures that are indicative of their eruptive setting. Therefore, textural studies of ancient igneous rocks can provide information of the presence of near-surface volatile reservoirs.

Specifically, studies that would be performed on returned ancient igneous rocks that will provide unique information on martian volatile history would include textural/petrologic investigations of the primary igneous minerals (relates to emplacement setting, and volatile history of magmatic source regions), mineralogical characterization of any secondary alteration products (relates to the environment and physical conditions under which the alteration took place, e.g., whether secondary minerals are "palagonites" or well-ordered clay minerals), and detailed chemical and isotopic characterization of the alteration products, the source rock, and any volatiles derived from the primary or secondary phases (relates to the chemistry and history of the volatile reservoirs involved in the alteration, as well as the volatile history of the magmatic source region). These kinds of studies would involve the extensive use of optical microscopy, scanning electron microscopy (SEM), electron microprobe, transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), and gas source mass spectrometry, to name a few. Also, insight into the ancient magnetic field of Mars, which has important implications for early atmospheric loss by sputtering,

could be gained from these samples. Numerous investigations could be performed on samples on the order of 10 g in size, and (for example) multiple 10–20-g samples are preferable to a single 200-g sample. As a case in point, I note the large amount of data collected on the 12-g SNC meteorite QUE 94201 (see LPSC XXVII abstracts, 1996). Studies of relatively unshocked samples are preferable, but this is not a strict requirement as it may be difficult to achieve in the ancient cratered highlands.

Impact processes supply samples of materials to planetary surfaces that might otherwise be unavailable at the surface due to burial or deep emplacement. Since deeper crustal rocks will likely show different effects of interaction with crustal volatiles than ancient igneous rocks that were emplaced at or very near the surface, studies of impact breccias are important. For example, deep crustal rocks may preserve evidence of Noachian hydrothermal activity, which will give insight into ancient volatile cycling on Mars. In addition, early, now buried sediments may be preserved in these samples. The types of measurements and questions addressed by the studies of ancient impact breccias are very similar to those outlined above for ancient igneous rocks. If breccias are to be collected, it is desirable to collect samples with dimensions larger than the size of the individual clasts, or if sampling of individual clasts is to be performed, documentation of the relationship of the samples to the "hand-sample"-sized source rock is necessary.

Shocked rocks may also preserve direct samples of past martian atmospheres since the shock process implants atmospheric constituents into rock samples. The classic example of this is the shock-melted pockets in shergottite EETA 79001, which reproduce with astonishing accuracy the composition of the current martian atmosphere (see Fig. 1) [e.g., 3]. Laboratory experiments have shown that this implantation can occur even when extensive shock melting does not [3], therefore any samples of shocked rocks have some possibility

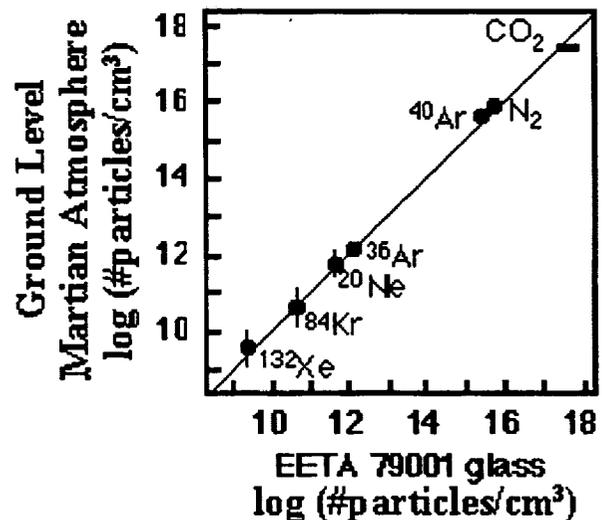


Fig. 1.

of revealing information about martian atmospheric chemistry in past epochs.

A final word about sample preservation requirements: At least some of the alteration minerals that will provide the most information on ancient climates begin to lose volatiles at temperatures below 100°C and completely break down at temperatures <250°C. Therefore, if using volatile-bearing alteration products to constrain the early climate history of Mars is among the primary goals of a sample return mission, care should be taken to maintain the sample in a low-temperature environment (>50°C, if possible).

References: [1] Pepin R. O. and Carr M. H. (1992) in *Mars*, Univ. of Arizona, Tucson. [2] Baker V. R. et al. (1992) in *Mars*, Univ. of Arizona, Tucson. [3] Wiens R. C. and Pepin R. O. (1988) *GCA*, 52, 295–307.

Viewgraphs presented at meeting—

Martian Climate—Reasonable Goal

Determine if Mars was once warmer/wetter or both, and the length of time this environment persisted

In order to do this we must:

- ❖ Understand the composition and distribution of current volatiles
 - ◆ atmospheric sample
 - ◆ soils
 - ◆ young rocks (e.g., SNC meteorites)
- ❖ Study the ancient rock record
 - ◆ samples of ancient igneous rocks
 - ◆ samples of ancient sedimentary rocks
 - ◆ impact breccias

For a cost-constrained mission, the most reasonable site is old terrain with rocks that may have formed during a warm/wet epoch

Ancient Igneous Rocks

Purpose:

Constrain conditions under which igneous rocks were emplaced and their subsequent interaction with surface/subsurface volatiles

Issues:

Eruptive setting

Amount/conditions of alteration

Chemistry of altering fluids

Comparison with younger igneous rocks (i.e., SNCs)

Types of measurements:

Search for evidence of magma/water interaction

Mineralogical characterization of alteration (SEM, TEM, etc.)

Chemical/isotopic characterization of alteration and source rock

Sample requirements:

~10-g fragments of numerous igneous units

Ideally, samples should be unshocked (this may be tough)

Storage/preservation: ~Mars ambient temperature or colder

Sample selection:

Possibly search for samples that are altered to varying degrees using (for example) *in situ* IR spectroscopy

Will need to be able to expose "fresh" rock surfaces

Ancient Impact Breccias

Purpose:

Sample numerous rock types that may not be otherwise accessible at the surface

Science issues:

Rocks from deeper crustal levels may retain evidence of hydrothermal activity or early sedimentation

Do these samples reflect two types of alteration: deep and surface?

Sample issues:

Types of measurements and preservation same as for other rock types

Need "hand-sample"-type rocks with dimensions larger than individual clasts

On-site characterization: Will it be difficult to determine whether a rock is a breccia before collection?

Igneous Rocks/Impact Breccias

Purpose:

Constrain composition of early martian atmosphere

Types of samples:

Rocks containing shock-melted pockets

Measurements:

As in EETA 79001 glass

Note that ancient impact glasses may not be preserved, but this has climatic implications

Donald D. Bogard, Johnson Space Center—

Martian Volatiles and Isotopic Signatures

Introduction: Data on martian volatiles comes from various sources:

- ❖ Viking atmosphere measurements
- ❖ modest groundbased spectra
- ❖ shock-implanted atmospheric gases in martian (SNC) meteorites
- ❖ trapped mantle(?) gases in martian meteorites
- ❖ volatile-rich solid phases in martian meteorites (hydrates, carbonates, sulfates, etc.)

Figure 1 compares measurements of several volatile isotopic species made on Mars by Viking against measurements made in glass inclusion produced by impact in the EETA 79001 martian meteorite. The close similarities between the two gas reservoirs across 8 orders of magnitude in gas concentrations constitutes a strong argument for the martian origin of this meteorite.

Figure 2 compares the $C^{36}Ar$ ratio against the $N^{36}Ar$ ratio for several solar system reservoirs: the Sun, lunar regolith, E (enstatite) chondrites, C1 and C3V carbonaceous chondrites, and the atmospheres of the Earth, Venus, and Mars. The lower $N^{36}Ar$ value for Mars is that actually measured by Viking, and the larger value is that estimated for early martian history prior to fractionated loss of N from the martian atmosphere. The ~5 order-of-magnitude spread in both these ratios suggests that the ratio of noble gases to chemically active volatiles on Mars could be quite variable, depending on the various sources for martian volatiles.

Data and models presented in this talk come from many sources. Apologies are given for the fact that no acknowledgments or literature citations are given.

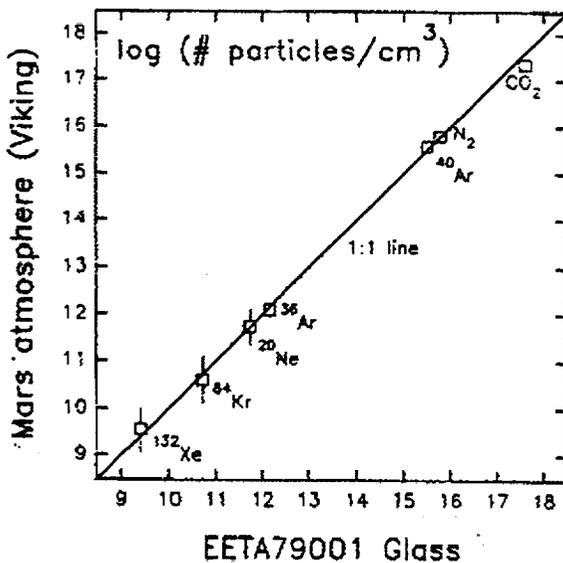


Fig. 1.

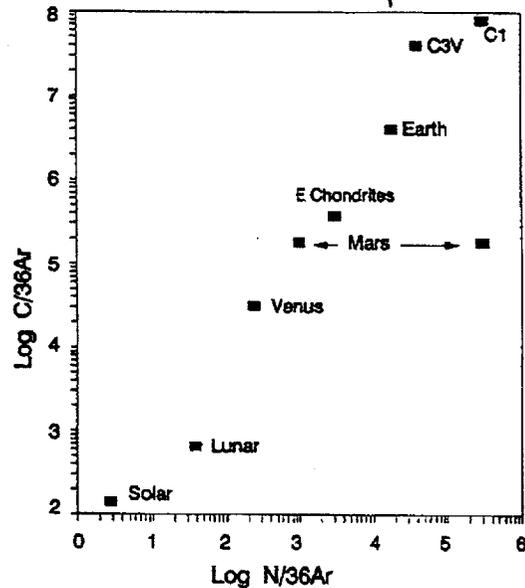


Fig. 2.

Atmospheric Volatiles:

Some important questions about martian atmospheric volatiles.

- ❖ What were the sources of martian volatiles? (e.g., mantle outgassing, solar, comets, cosmic dust)
- ❖ How do isotopic signatures characterize atmospheric loss mechanisms?
- ❖ How much water was lost and when?
- ❖ How have atmosphere-surface exchanges buffered volatile loss?
- ❖ What other martian processes are revealed in atmosphere? (e.g., outgassing, exchange reactions, nuclear interactions, etc.)

Some martian atmospheric components show isotopic mass fractionation that is indicative of significant early loss from the upper atmosphere:

D/H ($^2H/^1H$)	5x enriched over Earth
$^{15}N/^{14}N$	~60% enriched over Earth
$^{38}Ar/^{36}Ar$	~30% enriched over Earth
Xe isotopes	136/130 enriched 16-25% over chondrites and solar

$^{13}C/^{12}C$ and $^{18}O/^{16}O$ resemble Earth's, resolution poor

Several physical models have been offered to account for volatile loss and mass fractionation.

- ❖ Hydrodynamic escape of H
 - ♦ H possibly formed by reaction of abundant water with Fe^{+2} (may imply kilometer-deep oceans)
 - ♦ H loss by solar UV entrains other volatiles
 - ♦ Process occurred very early
 - ♦ Volatiles other than Xe are lost; remaining Xe is strongly mass fractionated

- ♦ Volatiles lighter than Xe were added later
- ♦ Later volatile source could be interior outgassing or late-stage accretion?
- ❖ Sputtering from upper atmosphere
 - ♦ Sputtering is driven by the solar wind and solar UV
 - ♦ Because species scale height is mass dependent, lighter isotopes are preferentially removed
 - ♦ A longer-term process compared to that above, but can fractionate H, C, O, N, A
- ❖ Dissociative recombination or photochemistry
 - ♦ Primarily affects N and O

Martian atmospheric noble gases give conflicting isotopic patterns, which indicate multiple origins for these volatiles. Figure 3 compares the isotopic compositions of Xe in the martian atmosphere, the Earth, chondritic meteorites, and the Chassigny (martian) meteorite against the solar component, which plots as a horizontal line. The Xe composition of martian atmosphere (shock implanted into EETA 79001) is quite different from the Xe composition of Chassigny, and the latter closely resembles the solar composition. One can speculate that martian atmospheric Xe may have been derived by mass fractionation of either the chondritic or solar composition.

Figure 4 compares the isotopic composition of Kr in the martian atmosphere, carbonaceous chondrites, and the solar composition against the Earth's composition, the latter being plotted as a horizontal line. Martian atmospheric Kr resembles solar, except for an enhancement at mass 80, which is probably a neutron-capture effect on Cl. In addition, the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio for the martian atmosphere may have a value as small as ~ 3.5 , much lower than values of ~ 5.3 – 5.6 typical of other solar system reservoirs. Thus, Ar in the martian atmosphere resembles atmospheric Xe in that its lighter isotopes are relatively depleted compared to solar or chondritic components, whereas lighter isotopes of Kr are enriched compared to chondritic Kr and similar to solar Kr. The isotopic composition of martian Ne is too poorly known to make any detailed comparisons.

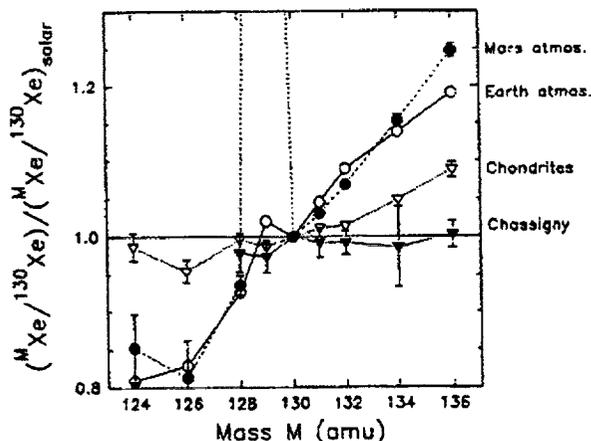


Fig. 3.

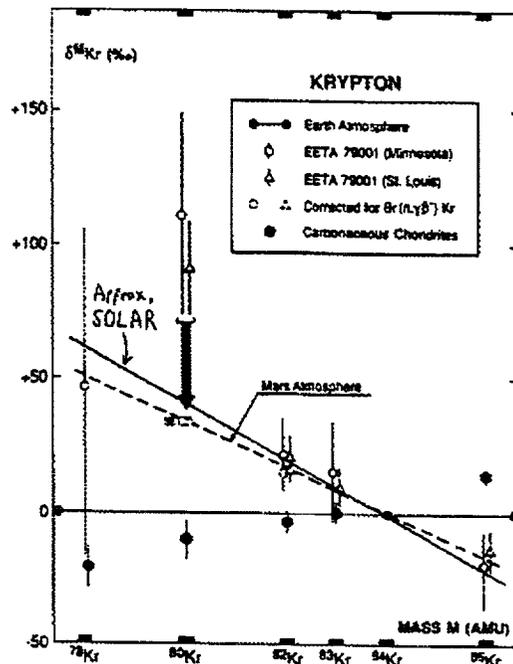


Fig. 4.

Other volatile components measured in some martian meteorites are not believed to have been shock implanted from the atmosphere, but rather to represent mantle gases. The solar like Xe in Chassigny is one such component, and an analogous mantle component may exist for Ar. Figures 5 and 6 present the case for two components of martian N. Meteorite analyses shown on both plots define mixing lines that pass near the martian atmospheric composition measured by Viking and the composition of the Earth's atmospheric N. Note that Figures 5 and 6 plot deviations of $^{15}\text{N}/^{14}\text{N}$ from a terrestrial standard ($\delta^{15}\text{N}$) against the $^{36}\text{Ar}/\text{N}$ and $^{40}\text{Ar}/\text{N}$ ratios respectively.

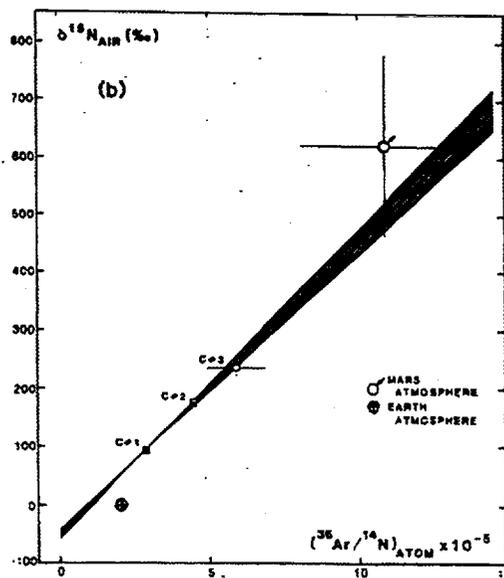


Fig. 5.

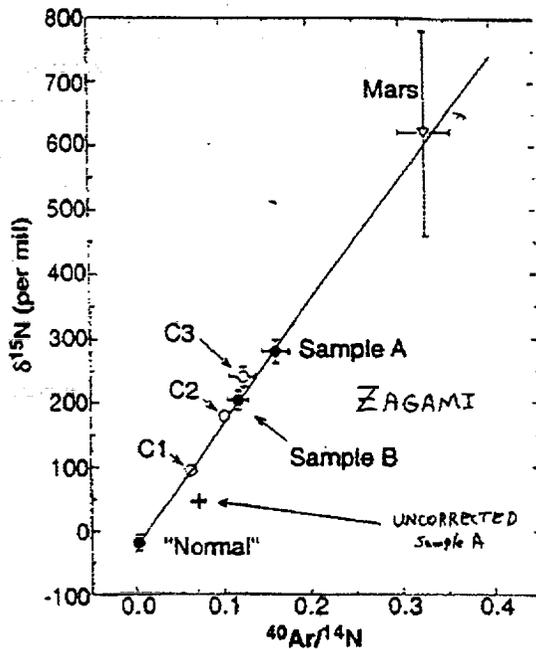


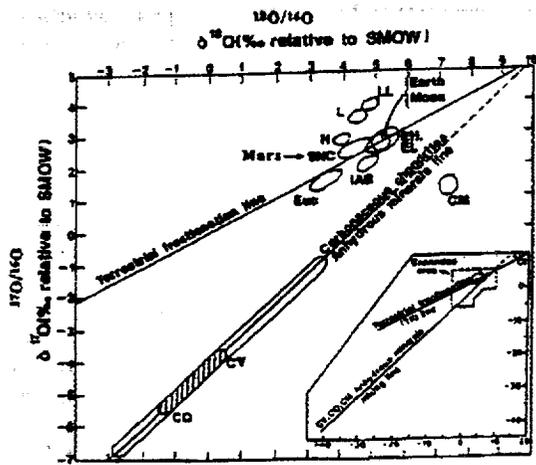
Fig. 6.

Surface Volatiles:

Some important questions about martian surface volatiles.

- ❖ What are the martian, near-surface, volatile-rich minerals?
- ❖ When and how did these volatile-rich species form?
- ❖ What isotopic equilibria exist among rock-surface-atmosphere?
- ❖ Do organics exist in these phases?
- ❖ The questions above under atmospheric volatiles also apply.

Measurements of martian meteorites have revealed several aspects about non atmospheric martian volatile elements. The oxygen isotopic composition of silicates differs from other solar system



The relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ for the Earth and the various meteoritic groups (figures adapted from Clayton et al., 1976; Clayton 1977; Anders 1967).

Fig. 7.

reservoirs (Fig. 7). Small quantities of volatile-rich phases such as clays, carbonates, sulfates, amphibole, chlorite, and mica all have been reported present in martian meteorites. How and when did these phases form? Abundant carbonate (~1% $(\text{Ca,Mg})\text{CO}_3$) existing in ALH 84001 probably formed from groundwater. Because this martian meteorite was dated at 4.0–4.5 G.y. old, the carbonate could derive from an early period of Mars. In contrast, water-bearing clay minerals in the martian nakhlite meteorites must be <1.3 G.y. old, for that is the dated formation time of these rocks (see later discussion).

An important question is whether O, C, and other volatile elements within martian meteorites are in isotopic equilibrium or disequilibrium. Disequilibrium would indicate the requirement for more than one volatile source. To address this question, we must understand that the $^{18}\text{O}/^{16}\text{O}$ ratio naturally fractionates among phases in equilibrium, depending on the species present and the temperature. This is demonstrated in Fig. 8 for CO_2 and H_2O in equilibrium with basalt. At 1000°C all three phases have very similar $^{18}\text{O}/^{16}\text{O}$, but at 0°C this ratio in CO_2 and H_2O differs by more than 4%, or >40‰. (This isotopic difference would be written as $\delta^{18}\text{O} > 40\text{‰}$, where δ indicates deviation of the $^{18}\text{O}/^{16}\text{O}$ ratio from a terrestrial standard. The notation $\Delta^{17}\text{O}$ indicates deviation of ^{17}O from the terrestrial fractionation line. The specific values of $\delta^{18}\text{O}$ for CO_2 and H_2O relative to the basalt depends on the $\text{CO}_2/\text{H}_2\text{O}$ mixing ratio.

Figure 9 is a plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ for various martian phases. The sloped line is the expected mass fractionation line for species in equilibrium. Silicate samples from martian meteorites plot in the relatively narrow region of $\delta^{18}\text{O} = \sim 3\text{--}5\text{‰}$. However, separated

$$\Delta^{17}\text{O} \equiv \delta^{17}\text{O} - 0.52 \delta^{18}\text{O}$$

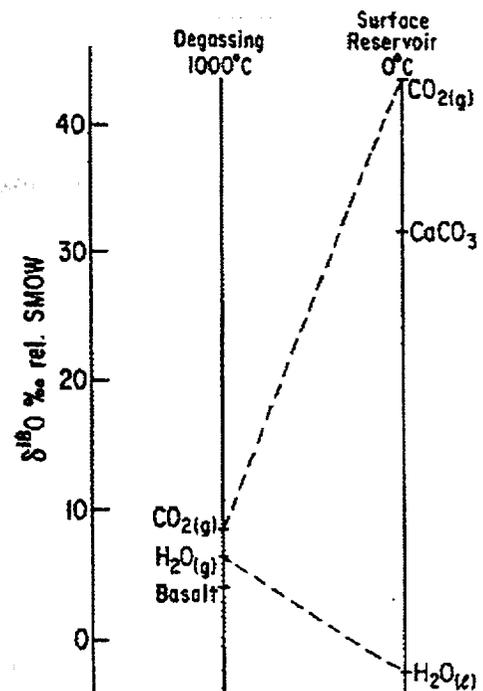


Fig. 8.

Oxygen Isotope Analysis of SNC Meteorites and Their Components

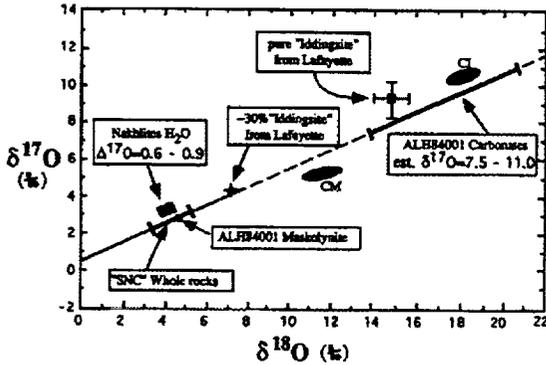


Fig. 9.

samples of the clay "mineral" called iddingsite plots at considerably higher values of $\delta^{18}\text{O}$, and may have a value of $\delta^{17}\text{O}$ that falls above the martian fractionation line. Water collected by high-temperature pyrolysis of nakhilites shows a $\delta^{18}\text{O}$ similar to martian silicates, probably as a result of high-temperature exchange. These data suggest that martian surface water may not be in isotopic equilibrium with mantle-derived silicate material, and may be evidence for an additional surface component, with a composition possibly similar to that of CI chondrites (Fig. 9).

Figure 10 compares the $^{13}\text{C}/^{12}\text{C}$ ratio plotted as $\delta^{13}\text{C}$ in ‰ notation compared to terrestrial carbonate for the carbon cycle of both Earth and Mars. On Earth, $^{13}\text{C}/^{12}\text{C}$ shows only modest fractionation effects (<10‰) among the major reservoirs of carbonate,

atmosphere, and mantle. Organic material on Earth shows a $\delta^{13}\text{C}$ value ~25‰ lower. With the exception of carbonate from ALH 84001, the abundances of carbon-containing phases in martian meteorites are very low (sometimes only ~10 ppm), and the phase being measured in many cases is rather uncertain. Nevertheless, measurements of martian meteorites indicate a much wider range of $\delta^{13}\text{C}$ compared to the Earth. In addition to the ALH 84001 data, carbonates measured in other meteorites suggest a range of $\delta^{13}\text{C}$ at least as large as -5‰ to +30‰. A sample with high-temperature C release was considered to represent mantle C and gave a $\delta^{13}\text{C}$ of ~-25‰. The $\delta^{13}\text{C}$ measured by Viking for the martian atmosphere was ~-10‰, but with the very large uncertainty of $\pm 50\%$. One measurement in EETA79001 was interpreted to be atmospheric CO_2 and gave $\delta^{13}\text{C}$ of ~-40‰.

Both the oxygen and carbon isotopic compositions of martian materials could be consistent with two or more volatile reservoirs that are not in isotopic equilibrium. These different reservoirs could represent separate components accreted to Mars or components produced by mass-fractionated loss processes discussed above. In addition, the D/H (or $^2\text{H}/^1\text{H}$) ratio measured in water released from certain igneous minerals contained in martian meteorites is greatly enhanced, up to about 5× Earth's ratio, and variable among different samples. The maximum enrichment $\delta^2\text{H}$ observed in martian meteorites is about the same as that observed in Earth-based spectra taken of the martian atmosphere. This could imply that isotopic exchange has occurred between atmospheric hydrogen and water in these igneous minerals. Because some phases show $\delta^2\text{H}$ ratios only about twice that of the Earth, the martian interior presumably contains a D/H ratio much lower than the atmosphere.

To summarize the case with martian volatiles, isotopes of H, N, Ar, Xe, C, and O all suggest two (or more) distinct volatile components. One is interior and presumably reflects volatiles accreted with Mars. The others are probably surface and atmospheric components, produced either by heterogeneous late-stage accretion or mass fractionation during atmospheric loss, or both. Among the possibilities for accreted components are CI chondrite material, comets, and cosmic dust. Because of fractionation mechanisms, most martian volatiles probably show a temporal variation in isotopic composition. Apparent existence of nonequilibrium volatile components on Mars in the recent past may indicate the lack of significant crustal subduction to mix these components. Analyses of martian-returned volatile-rich phases could greatly help in our understanding of these issues.

Isotopic Chronologies:

Some important questions about martian isotopic chronologies.

- What are the ages of major geological terrains on Mars?
- ❖ What is the timescale of active volcanism?
- ❖ What is the timescale of major impact cratering? (must date surfaces to calibrate crater count ages)
- ❖ Were early impacts related to water erosion of surface?
- ❖ What terrains were sampled by martian meteorites?
- ❖ How do initial ratios characterize rock petrogenesis?

Because martian meteorites reveal groupings in their isotopic chronologies, we discuss them in this manner. Figures 11 and 12 show isochron plots of the ^{87}Rb - ^{87}Sr and ^{147}Sm - ^{143}Nd isotopic systems, respectively, for several shergottites, two nakhilites, and ALH 84001. These figures can be used as reference for some of the characteristics listed below.

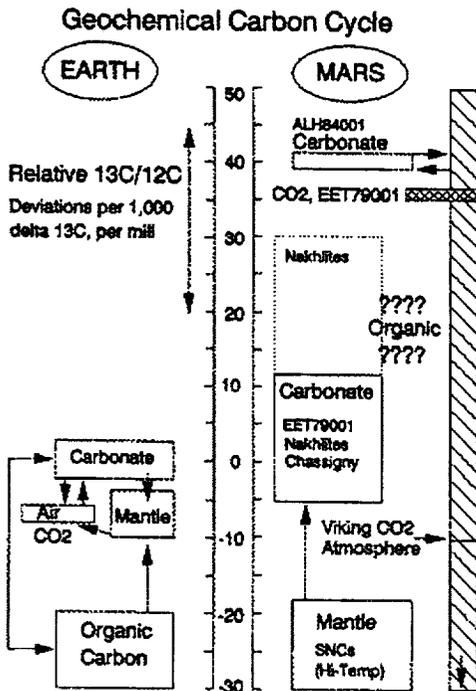


Fig. 10.

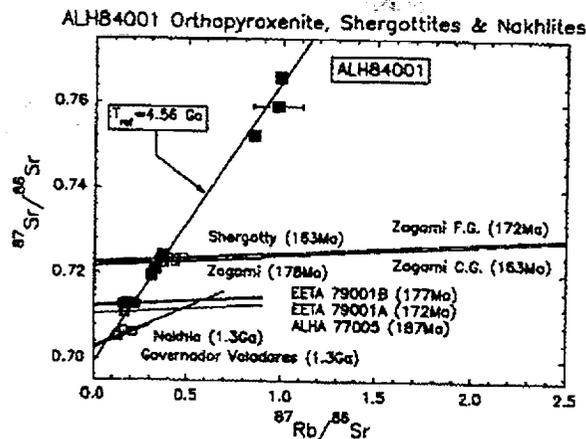


Fig. 11.

Characteristics of shergottite meteorites.

- ❖ All are appreciably shocked.
- ❖ They have model isotopic ages of ~4.5 Ga, which indicate an early initial differentiation of the planet. This also suggests minimal crust recycling compared to Earth.
- ❖ Some Sm-Nd whole-rock "isochron" ages suggest ~1.2 Ga.
- ❖ All show Rb-Sr, Sm-Nd, and Pb-Pb ages of ~0.17 Ga.

All shergottites are linked by the above characteristics. However, their mineralogies and initial isotopic ratios differ considerably. The latter suggests that they were not cogenetic 0.17-Ga ago, and they probably had a complex prior history. The nature of the ~0.17-Ga event is not completely defined and may have involved impact melting, igneous, and/or rock assimilation processes. Spectra signatures of the shergottites are similar to the Mars' uplands, suggesting that their composition may be common on Mars.

Characteristics of nakhilites and Chassigny.

- ❖ Live ^{146}Sm (half-life 10^3 Ma; decays to ^{142}Nd) was present in the source rocks. The $^{142}\text{Nd}/^{144}\text{Nd}$ ratio is greater than the lunar value and suggests an even earlier mantle differentiation for Mars compared to the Moon.

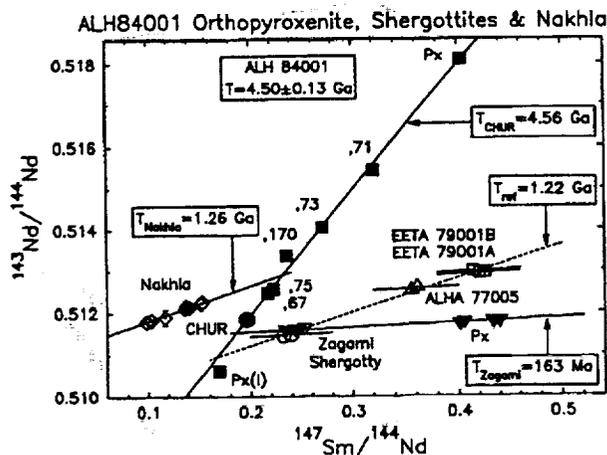


Fig. 12.

- ❖ All give isochron ages of 1.3 Ga by Rb-Sr, Sm-Nd, K-Ar, and/or U-Pb. (Does the similarity in this age and the ~1.2-Ga Sm-Nd model age of the shergottites suggest a relation?)

- ❖ None are significantly shocked.

Their initial isotopic ratios are similar, unlike shergottites. (See Longhi's presentation for the significance of initial ratios.)

The nakhilites and Chassigny are linked by the above characteristics. They likely had an igneous origin 1.3 Ga ago. They likely were ejected from Mars in a common event ~12 Ma ago, which is their cosmic-ray (space)-exposure age.

Characteristics of ALH 84001 (orthopyroxenite with carbonates).

- ❖ The Sm-Nd model age is ~4.57. Live ^{146}Sm possibly existed.
- ❖ Rb-Sr and Sm-Nd isochron ages are ~4.5 Ga.
- ❖ K-Ar (^{39}Ar - ^{40}Ar) age is 4.0 Ga and may represent impact resetting.

In many respects, ALH 84001 differs from the other martian meteorites.

Chronology Summary: Isotopic chronologies signify very early mantle differentiation for Mars. However, most martian meteorites have rather young (<1.4 Ga) isotopic ages. Most of these ages appear igneous, but some may reflect effects of impact melting. Young isotopic ages are not obviously consistent with the interpretation from crater densities that most of Mars' surface is much older.

Energetic Particle Interactions:

Some important questions about energetic particle interactions.

- ❖ Martian meteorites give information about Mars' near-surface rocks. Questions about their ejection from Mars are: How? When? Where? How many events?
- ❖ How can nuclear reaction products (stable and radioactive) in Mars surface samples help define the past density of Mars' atmosphere if it experienced time-variable shielding?
 - Weathering rates of exposed rocks
 - Mixing rates of regolith

To fully use the characteristics of martian meteorites to make inferences about Mars, we need to understand the origins of these samples. None of the martian meteorites resided for a significant period at the martian surface, for none show evidence for irradiation by cosmic rays on Mars. Exposure ages in space for the martian meteorites range over ~0.6–15 Ma, and show at least three and possibly as many as five groupings of these ages. Theoretical models suggest that relative large crater(s) are required to eject these meteorites into space (~10–100 km diameter, depending on the size of the objects ejected).

Two viable models exist for explaining the space exposure ages of martian meteorites. One assumes that separate cratering events on Mars ejected those meteorites with a common exposure age. This explanation would require at least two events to eject the shergottites and one event to eject the nakhilites and Chassigny, and all three craters would have had to occur in relatively young (<1.4 Ga) and presumably rare martian terrain. The second explanation assumes that all martian meteorites were ejected in one very large cratering event, and that the space exposure groupings were formed by later collisional break-up events in space. Figure 13 schematically shows one variant of this model whereby all shergottites were ejected

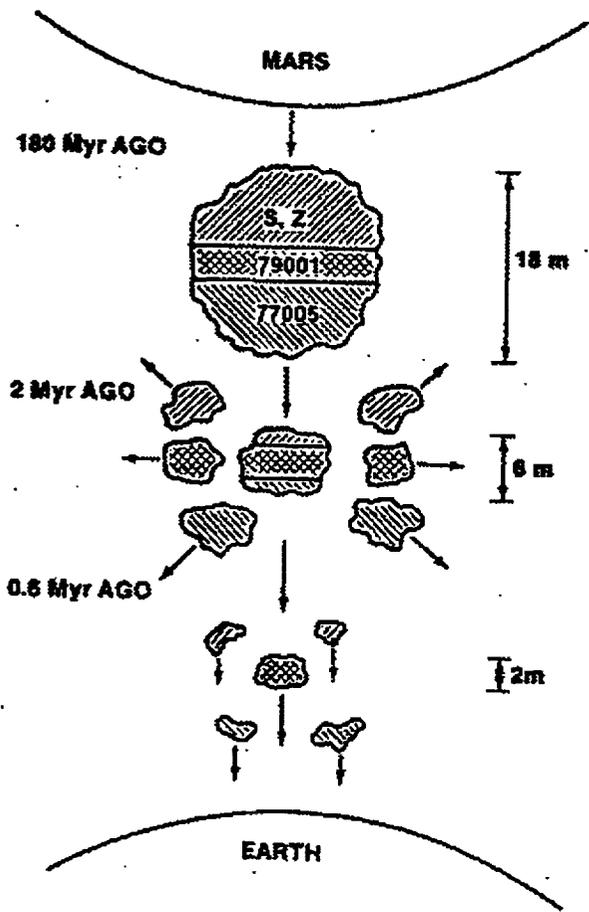


Fig. 13.

~0.18 Ga ago as a large shielded block, which was collisionally disrupted into smaller fragments ~3 Ma and ~0.6 Ma ago. This scenario permits only a single impact into young terrain, but requires a very large crater, which may not exist. Various combinations of these two exposure models and of the ejection time in model 2 can also be envisioned.

Although the martian meteorites give no evidence of energetic particle irradiation on Mars, the present rarefied martian atmosphere allows entry of cosmic-ray particles, which undoubtedly produce nuclear products at the martian surface. The quantity of the products produced are dependent upon the specific product and the total shielding offered by the atmosphere and surface material overlying the sample. Nuclear products produced by energetic primary and secondary particles show a maximum in their production at a shielding depth of ~0–50 g/cm², whereas nuclear products formed by thermalized neutrons reach a maximum concentration at a shielding depth of ~200 g/cm² (Fig. 14).

In principle, differences in production rates of various nuclear products as a function of shielding might be used to reveal certain aspects of martian surface history:

- ❖ An earlier epoch of a dense martian atmosphere. This possibility assumes that an early atmosphere was dense enough to effectively shield the surface, which, because of the different chemical composition of atmosphere and rock, would greatly decrease the production of certain

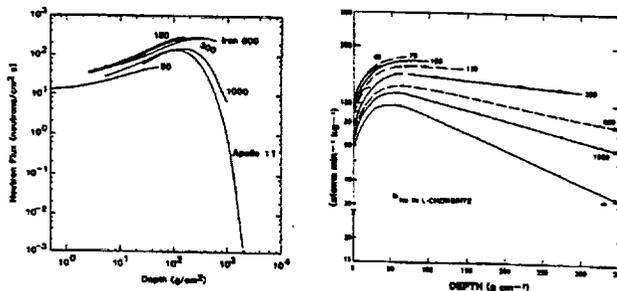


Fig. 14.

nuclear products over that time. Thus, if the atmosphere contains less-stable nuclear products (e.g., ²¹Ne) than expected, that might indicate an extended period with a dense atmosphere. In addition, some ratios of cosmogenic nuclides (e.g., ⁸⁰Kr/⁸²Kr) are shielding dependent. It was noted above that atmospheric Kr trapped in EETA79001 seems to have an enhanced abundance of ⁸⁰Kr.

- ❖ Regolith mixing rates. Measurements of core samples returned from the Moon yielded significant information about the formation and mixing rates of fine-grained material within a few meters of the surface. Lunar surface rocks gave information on their times of excavation to the surface via impact cratering. Similar kinds of information can, in principle, be obtained from martian surface material.

Summary of Martian Meteorites: Martian meteorites represent petrologically diverse rock types. Several contain volatile-rich alteration products and shock-implanted martian atmosphere. Returned samples from the martian surface, however, are likely to contain even greater quantities of these and other volatile-rich, alteration products, possibly including evaporate deposits. Most martian meteorites show relatively young formation or impact events, with ages of ~0.17 Ga and ~1.3 Ga. All show space-exposure ages of ~0.6–15 Ma, in three or more age groupings.

Exposure and Crystallization Ages of Martian Meteorites

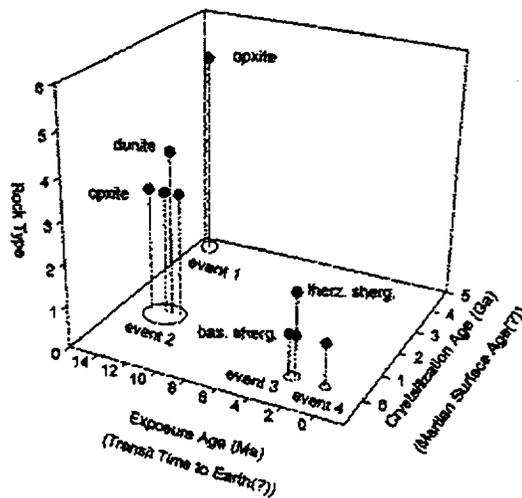


Fig. 15.

We can think of the martian meteorites as analogous to approximately three Mars sample return missions that collected only subsurface rocks within a limited area. Petrologically, martian meteorites represent five different rock types. These show three major groups of isotopic ages, ~ 0.17 Ga, ~ 1.3 Ga, and ~ 4.0 – 4.5 Ga (ALH 84001), and at least three groups of space-exposure ages. Meteorites sharing one or more of these characteristics have an implied linkage, and the greater the number of these three characteristics shared by two or more meteorites, the greater the probability that they derived from a common area of Mars, i.e., that they are equivalent to a single limited sample return. This relationship is illustrated by Fig. 15, which plots the three parameters, rock type, formation age, and space-exposure age against one another for those meteorites for which these data are available. In such a plot, the three sample groupings become obvious. Although the shergottites show

two rock types (basaltic and lherzolitic), these are believed to be closely related. All shergottites show a common isotopic chronometer age of ~ 0.17 Ga, and all except EETA79001 have very similar space exposure ages. Each difference has a reasonable explanation that does not preclude all the shergottite meteorites deriving from a limited area of Mars. Similarly, the nakhlites and Chassigny show similar isotopic formation ages and space exposure ages, even though Chassigny represents a different rock type. Meteorite ALH 84001 by itself forms a third group. It is a different rock type with a distinctly different isotopic formation age, and it may or may not share a common space exposure age with group 2.

If each of these three groups of martian meteorites indeed represents a separate impact ejection event from Mars (see above), then this perspective may give some insight to the diversity of subsurface rock types available in a limited sampling area of Mars.

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Geology Resources

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What the SNC Meteorite Tells Us about Mars

It is widely, though not universally, accepted that the SNC (shergottites-nakhlites-chassignites) meteorites come from Mars. These basaltic achondrites have traces of water-bearing minerals and magnetite, which indicates that their oxidation states are similar to terrestrial basalts, yet their oxygen isotope compositions show that they are definitely extraterrestrial. Belief in a martian origin is based on relatively young (< 1.3 Ga) crystallization ages—such “recent” igneous activity being likely only on a planet large enough to retain its heat—and on a distinct isotopic signature of the martian atmosphere in Ne and Ar gas trapped in an impact-melted glass in one of the shergottites. As with all basaltic rocks, the SNCs provide constraints on the composition, structure, and evolution of their parent body.

Composition of the Surface and Interior: Most of the SNCs are medium- to coarse-grained rocks that may have gained or lost crystals during slow solidification; so, unlike fine-grained basalts, bulk chemical analyses do not recover their parent magma compositions. Fortunately, a large database derived from melting experiments allows us to estimate the composition of the parent magmas from the mineral compositions measured in the meteorites. Estimates of the parent magma compositions of the SNCs show that martian lavas have a wide range of low Al_2O_3 and high FeO concentrations with an average that is comfortably close to those of the Viking Lander soil analyses. Melting experiments also tell us that FeO is fractionated only weakly during planetary melting and limited subsequent crystallization of magma near the surface, so the average FeO concentration (~18 wt%) in the SNC parent magmas is probably a good approximation of the FeO concentration in the martian mantle. This value is more than twice that of the Earth’s upper mantle. Another constraint on martian composition comes from the SNC K/La ratio, which is less than chondritic, but nearly

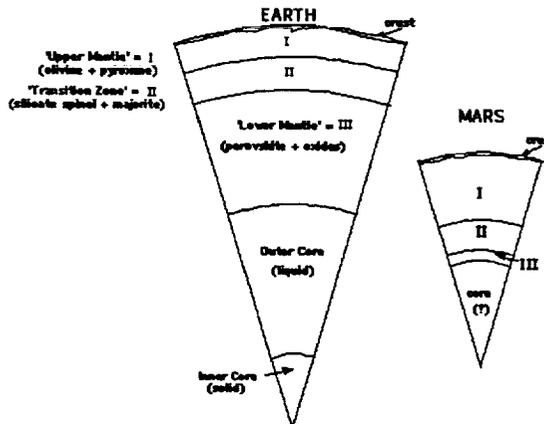


Fig. 2. Comparison of the internal structures of the Earth and Mars to scale. Regions I, II, and III refer to olivine + pyroxene, spinel + majorite, and perovskite + oxides, respectively.

twice as high as the Earth’s. Because K and La are both highly incompatible elements, their ratio changes very little during most igneous processes, yet bulk K abundance is likely to vary from planet to planet because of its moderate relative volatility, whereas all the rocky planets are expected to have similar (i.e., chondritic) abundances of La and the other refractory elements (Ca, Al, Ti, Mg, Si, REE, U, Th). Thus the K/La ratio is an effective planetary probe that indicates that Mars has a richer endowment of the volatile elements (H, C, Na, S, P, etc.) than the Earth. Some of this endowment may have been spent, however, in oxidizing Fe that wound up as FeO bound in mantle silicates instead of metal in the core. Because the most likely oxidant is H_2O , it is possible that Mars is actually much drier now than the Earth. Relatively dry magmatism is also indicated by the relatively sparse alteration in the SNC meteorites and by the low OH content of SNC amphiboles (ion probe analyses reveal that only about 10% of the hydroxyl sites contain OH groups).

The total amount of S in Mars that is consistent with the SNC K/La ratio is far in excess of what could be in the martian mantle, so it is likely that much of the sulfur is in the core. This inference is consistent with estimates of relatively low mantle abundances for elements such as Ni, Co, and Cu, which have strong affinities for Fe metal and sulfide. Placing most of the inferred S in the core and accepting as a trial proposition that Mars has overall chondritic abundances of Fe and Ni allows the composition and size of the martian core to be computed by mass balance (78% Fe, 8% Ni, 14% S; 1700 km). Data on the inclinations of Mars’ axis of rotation obtained from the Pathfinder mission will yield an accurate moment of inertia that will be the first test of the geochemical model. A more

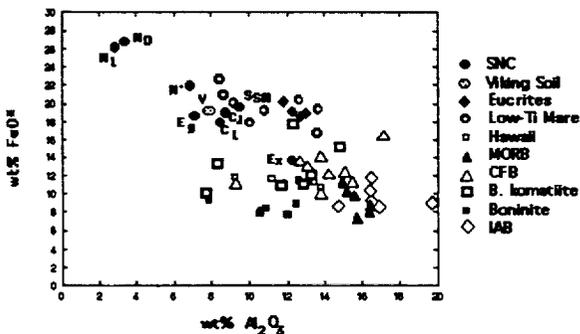


Fig. 1. Composition of SNC parent magma compositions with solar system hypersthene-normative basalts. N_D , N_L , N —Nakhlite; C_1 and C_L —Chassigny; E_1 and E_2 —EETA 79001A groundmass and xenocryst assemblage parent liquids; S_{SM} —Shergotty/Zagami parent liquid; V—Viking Lander soil analysis (normalized).

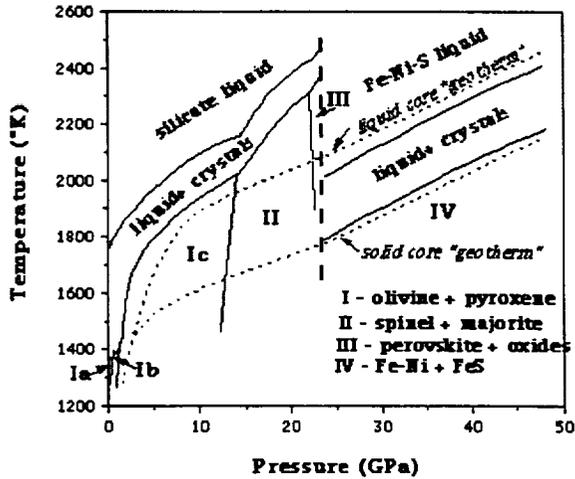


Fig. 3. Schematic phase equilibria relations for the Dreibus-Wänke Mars model and calculated temperature-depth relations. Subdivisions of region I refer to accessory aluminous phase: Ia—plagioclase; Ib—spinel $\{(Mg, Fe)Al_2O_4\}$; Ic—garnet. Dashed line marks core-mantle boundary for the preferred compositional model. Phase boundaries for core materials are calculated from freezing point depression equations for the Fe-FeS system.

rigorous test will come from seismic measurements (Mars InSight), which should allow direct determination of core size. Core composition also plays an important role in determining thermal structure. The absence of a significant martian magnetic field suggests that a strong core dynamo, driven by the release of latent heat of crystallization, is not operating. Thus, either the martian core is completely molten or completely solid; the liquidus of the core, which depends on the S concentration, provides a minimum temperature for a "hot" martian geotherm, while the core solidus provides a maximum temperature for a "cold" geotherm.

Magmatic Style: In addition to constraints on Mars' bulk composition and structure, the SNC meteorites provide insights into Mars' melting and differentiation processes. The low Al_2O_3 con-

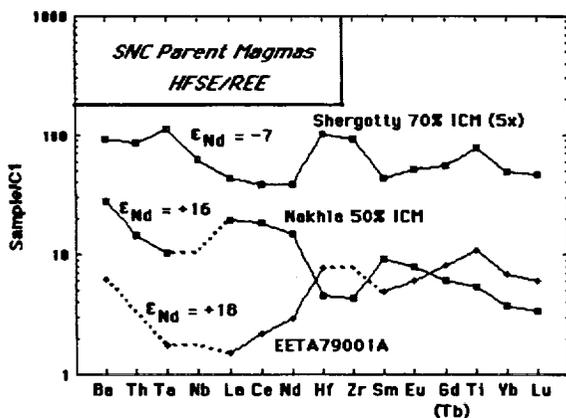


Fig. 4. Refractory incompatible element pattern of SNC parent magmas. Elements are arranged in order of increasing incompatibility from right to left. The Nakhla and Shergotty parent liquids are calculated using the indicated percents of intercumulus melt (ICM) and published weight partition coefficients between pyroxene and liquid. Values of ϵ_{Nd} are calculated for 0.18 Ga.

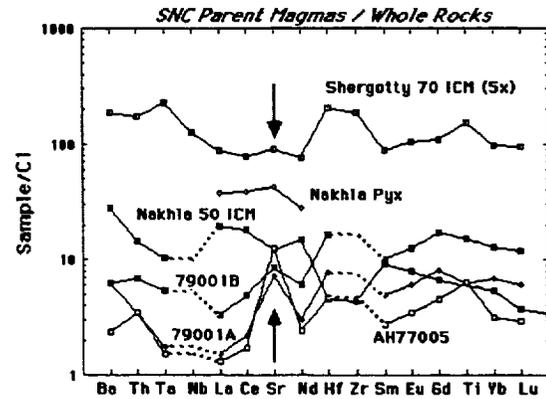


Fig. 5. Refractory incompatible element pattern of SNC parent magmas including. Elements are arranged in order of increasing incompatibility from right to left. The Nakhla and Shergotty parent liquids are calculated using the indicated percents of intercumulus melt (ICM) and published weight partition coefficients between pyroxene and liquid.

tents of the SNC parent magmas are consistent with differentiated source regions, either lunar style (magma ocean cumulates) or terrestrial style (depletion by basalt extraction). The absence of negative Eu-anomalies in the REE patterns of the SNC parent magmas obviates formation of an ancient anorthositic crust and complementary Al-poor mantle. Patterns of extreme depletion of the light REE in chondrite-normalized plots of the Antarctic shergottite REE abundances are consistent with multiple episodes of previous melt extraction. Because shock effects have disrupted some of the isotopic systems, crystallization ages for most of the shergottites remain ambiguous. One interpretation, supported by a Sm-Nd whole-rock isochron, is that most of the shergottites formed at the same time as the nakhlites and chassignites (~1.3 Ga) and were then remelted by an impact at ~0.18 Ga. Sm-Nd isotope systematics require that the nakhlite source region had long-term, strong light-REE depletion prior to melting. If 1.3 Ga was the time of shergottite formation, then Nd isotopes require that their source was long-term light REE enriched (crust) and that the observed patterns of light-REE depletion were produced in the melting process. Although

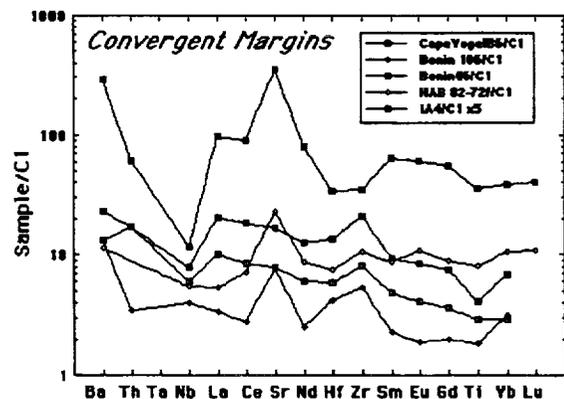


Fig. 6. Refractory incompatible element pattern of terrestrial volcanic rocks from convergent plated margins. Prominent spikes at Ba and Sr are thought to reflect enrichment of the source region by fluid transport.

improbable, variable amounts of fractional fusion could produce these relations. If 0.18 Ga was the crystallization age of most of the shergottites, then their source was similar to that of the nahklites, long-term REE-depleted, and the apparent 1.3-Ga whole-rock isochron is an artifact of assimilating a light REE-enriched component (crust?) into melt from a depleted mantle. Besides being more conventional, the 0.18-Ga scenario is also consistent with complementary trace-element patterns of rare earth and high field strength elements (HFSE = Nb, Hf, Zr) in nahklite and shergottite parent-magma compositions: It appears that a Nahkla-like melt component was extracted from the shergottite source prior to melting (Nd isotopes specifically prohibit this relation if the shergottites formed at 1.3 Ga). Another clue to martian magmatism lies with Ba and Sr abundances. Barium and Sr usually behave similarly to Th and Ce, respectively, yet in the Antarctic shergottites Ba and Sr are dramatically enriched with respect to Th and Ce. These enrichments in concert with nonchondritic ratios of HFSE to REE are characteristic of convergent plate-margin volcanics on Earth. This similarity presumably does not imply plate tectonics on Mars, but probably does suggest that fluids preferentially extracted Ba and Sr with respect to the REE and preferentially extracted REE with respect to the HFSE. Subsequently these fluids metasomatized depleted mantle, possibly fluxing melting in the process.

A final clue provided by SNC meteorites lies in the 4.50-Ga crystallization age of one shergottite (E84001). The very age of this

plutonic rock, which is apparently well constrained, is grounds for amazement—finding similarly old and intact pristine rocks on the Moon takes considerable effort. That the rock is relatively unaltered is also amazing in light of the popular notion of an ancient warmer, wetter epoch replete with hydrothermal activity on Mars. Most significantly, perhaps, is the implication that Mars' magmatic style did not change over geologic time: The texture and orthopyroxene composition indicate close affinities to the other shergottites, which are much younger. Thus Mars' crust may consist primarily of a pile of SNC-like volcanic and hypabyssal rocks with no distinction in composition between old crust and young volcanics, unlike the Moon or Earth. Of course, acceptance of this unique style of planetary differentiation is contingent upon finding more rocks with similar petrological characteristics.

In summary, the SNC meteorites tell us a great deal about Mars, and there will be even greater understanding once the moment of inertia and core size are measured accurately, but the SNCs' stories are inherently limited by the lack of geological context and by the potential disruption of isotopic systems and magnetic domains by shock in the impact events that blasted these rocks off Mars. Returned samples of igneous rock offer the potential of not only enhancing our understanding of the martian interior significantly, but also hold promise of calibrating the absolute ages of Mars' surface features—knowledge that should prove vital to any systematic plan of exploration.

Viewgraphs presented at meeting—

What the SNC Meteorite Tells Us About Mars

Rationale for Fresh Igneous Samples

Calibrate crater frequency models

Ancient magnetic field?

Provide better constraints on:

Planetary bulk composition and structure

Timing and nature of core/mantle/crust differentiation

SNC Meteorites

Shergottites: [ol, opx, aug] plg + plag; fine to medium grained; basaltic to poikilitic cumulate texture; 0.18 and 4.5 Ga

Nakhlites: aug + ol + plag; medium grained; porphyritic; 1.3 Ga

Chassigny: ol + aug; medium grained; cumulate; 1.3 Ga

SNC Parent Magmas

Major Elements

Parent-magma composition not preserved during transport and solidification

Parent magmas (PM) low in Al_2O_3 , high in FeO

❖ ~Viking soil analysis less S, Cl

PM derived by melting of differentiated sources

EETA 79001, ALHA 77005 → Shergotty, Zagami

Trace Elements

K/La → moderate volatile depletion

Core formation not as extensive as Earth's (W, Cr, Mo), but S is higher (Ni, Co, Cu)

Lithophile-incompatible elements show:

- ❖ Complimentary REE/HFSE patterns
- ❖ Crustal assimilation: EETA 79001 → Shergotty
- ❖ Similarities to terrestrial convergent plate margin lavas

Sampling Goals

A range of FRESH basalts →

Calibration of surface age(s)

Remnant magnetism

Parent magma compositions: style and timing planetary differentiation bulk composition and structure

Ancient crustal samples

Nature of the crust

Planetary differentiation

Bulk composition

Precursor Measurements

Axial precession rate → moment of inertia

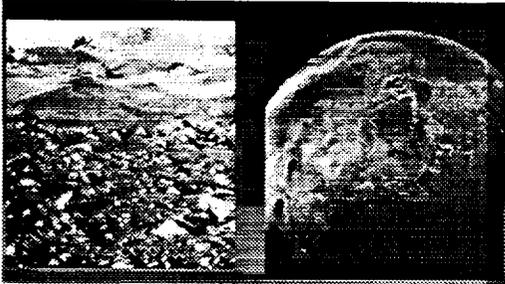
Seismic measurements → core size

Ron Greeley, Arizona State University—

Mars Sample Return: Goals for Geology

OMIT TO
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Mars history is complex



Summary for Geology

Samples are needed to date surfaces for calibration of crater counts; critical for stratigraphic framework of Mars

Multiple samples from multiple sites are needed to address martian diversity

Sand samples can provide insight into surface processes

New high-resolution data for landing sites would increase the scientific potential from samples

Mobility enhances sample-return missions

Calibration of crater "counts"

It will be a long time before all key units are radiometrically dated

Crater-counts are the principal means for "age-dating" unsampled surfaces

Used for comparing planetary and satellite surface histories

Lunar surface is the primary base, using Apollo samples and related crater counts

Extrapolation from Moon to Mars

Several models have been developed

Critical factors

- ❖ Gravity scaling
- ❖ Target properties
- ❖ Impact populations
- ❖ Gravitational focusing (Jupiter)
- ❖ Crater count methods

Large uncertainties in the martian timescale; implications for:

- ❖ Climate record
- ❖ Magmatic-volcanic history
- ❖ Tectonic events
- ❖ General evolution of interior and surface

Understanding surface processes and history

>50 major geologic units have been identified on Mars, representing a variety of processes and ages

Based mostly on remote sensing with limited “ground truth”

Many questions will probably remain, even after MGS, Pathfinder, Mars-96, MVACS:

- ❖ Has magmatic differentiation occurred; if so where, when, etc. (re: Longhi)
- ❖ Are the ridged plains (marelike units) volcanic in origin?
- ❖ Did oceans exist on Mars?
- ❖ Did glaciation occur?
- ❖ Are the valley networks the result of surface water or mass wasting?
- ❖ Etc.

Some key units for sampling

Memnonia Fossae Formation

- ❖ Polar deposits, or
- ❖ Eolian deposits, or
- ❖ Volcanic ash (ignimbrites)

Hesperian ridge plains

- ❖ Volcanic (marelike), or
- ❖ Sedimentary

Noachian ridged plains

- ❖ Volcanic (marelike), or
- ❖ Sedimentary

“Ancient crust”: important, but may be very difficult to obtain an unambiguous sample

Highland paterae: explosive volcanism?

Sand

- ❖ SEM analysis could provide insight into surface processes
- ❖ Glacial, aeolian, fluid, etc.
- ❖ Re: Kuenen, Krinsley, Marshal, etc.

Sampling strategies for geology

Scenario 1, “Grab-bag” approach (e.g., Mars Pathfinder)

Scenario 2, focus on “calibration” of crater counts

Scenario 3, focus on some key events in martian history

High-resolution remote sensing + surface mobility = better sampling

Multiple samples from multiple sites are required

Scenario 1: The “Grab-Bag Approach”

Has potential to sample wide variety (age and type) of rocks in local area

No guarantee that this will happen!

Context is not known; could be inferred, but without much confidence

Could lead to some interesting debates!



Scenario 2: Crater-Count "Calibration"

Complexities

Focus on key stratigraphic horizons

Homogeneous, widespread unit, easily identified

"Clean" crater counts (clearly superposed craters; surface not eroded, mantled, nor exhumed)

High probability of obtaining valid rock sample from which radiogenic age of unit can be obtained

Lunae Planum

- ❖ Marks the base of the Hesperian System
- ❖ However, it is inferred to be volcanic based on mare ridges, but could be of other origins
- ❖ Perhaps precursor mission (lander) could address origin before sample return

Scenario 3: Some Key Events in Martian History

Sampling to address:

Youngest volcanics (determine age and petrology); probably easiest to do

Oldest crust (determine age and petrology); probably very difficult to locate site with guaranteed access

Determine age(s) of outflow channels: need dateable samples that bracket channel formation;
some alternatives:

- ❖ Dateable impact ejecta for crater interleaved between channels
- ❖ Pillow basalts in channel (?? none identified, but something to seek)
- ❖ Dateable sediments (a long shot?)

Daedalia: a potential site

Young volcanics

Ancient crust

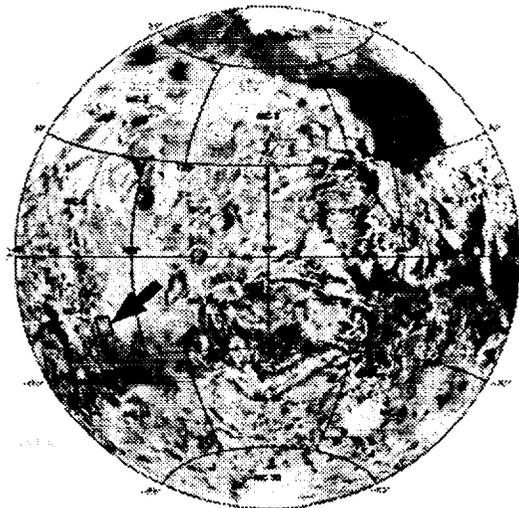
Outflow channel

Requirements

Precursor data

Accurate landing

Some mobility



Western Daedalia Planum

Sampling Rationale	Probability
Young volcanics; represents 603,000 km ²	High
Intermediate-age volcanics; represents 724,000 km ²	High
Central peak material; from 120-km-diameter impact crater; potential deep crust sample (>10 km depth)	Good
Surficial materials; windblown and possible fluvial materials	Moderate
Crater rim material; sample of less deep crustal material than central peak	Good

Geologic exploration/development on Earth

Reconnaissance (\$1000s)

- ❖ Orbital remote sensing (10s m)

Site selection (10,000s)

- ❖ Airborne surveys (submeter)

Site certification (\$100,000s)

- ❖ Aerial overflights, helicopter drop-off, ground work, etc.

Development (> \$Ms)

- ❖ Drilling, mining, etc.

The Field Geology Approach to Sampling

On Earth	On Mars
Reconnaissance RS (Laboratory) Overflight	- Remote sensing Regional Ultra-high-resolution
Initiate field work Helicopter drop-off Multiple drop-off	- Small landing ellipse Pinpoint landing Capable rover
Selective sampling	- Manipulators/tool kits

Conclusions

Dated samples from key units are required for the stratigraphic framework; in turn, this relates to the history and evolution of Mars

Samples are required to resolve geologic problems, such as styles of volcanism

Multiple samples from multiple sites are required

First sample site cannot solve all problems, but must be *interesting*

The science potential of a sample return mission is enhanced by high-resolution precursor data (for site selection) and mobility (for sample acquisition)

Allan H. Treiman, Lunar and Planetary Institute—

The Surface Materials of Mars

For a Mars 2005 sample return mission, both site selection and sampling strategies must consider the nature of the surface and near-surface materials of Mars. In simplest form, the surface of Mars consists of three fundamental units: dark, bright, and intermediate. Although named by their albedo in visible light, the units are also distinct in photogeology, thermal inertia, and radar reflection properties. The dark unit is interpreted to represent basaltic sands or outcrops, which are discussed elsewhere by H. McSween Jr.

The bright surface units are almost certainly dust. Bright material is deposited by global dust storms and redistributed on timescales of years by normal winds. Bright regions also have low thermal inertias, consistent with very fine grain sizes. The chemical composition of the martian dust was analyzed by the Viking landers, and is basaltic, very similar to some of the martian meteorites. The dust contains percent levels of sulfur. The mineralogy of the dust has been difficult to define. Variations in the VLXRF chemical analyses are consistent with varying proportions of titanomagnetite and of a magnesium sulfate. The VL magnetic properties experiment is consistent with titanomagnetite, and the VL biology experiments are consistent with abundant ferroan smectite, but the 2.2- μm absorption characteristic of clays has not been observed. IR and visible spectra are consistent with bulk and nanophase hematite and possibly ferric oxyhydroxides, and iron sulfates are possible. Absorptions from carbonate and sulfate minerals have been detected in IR spectra, but exact mineral identification has proved difficult. Carbonate absorptions are most consistent with a hydrous magnesium carbonate, but the sulfate absorptions are not diagnostic. Scapolite had been suggested as a possible surface mineral, but spectral and thermochemical data suggest that it is not a significant component of the dust. The dust contains percent levels of water, based on distinct O-H absorption features, but its mineralogic siting is not known [1]. The martian meteorites contain low-temperature alteration minerals that may be of significance for the dust. Among the alteration minerals are smectite, illite, and Ca- and Mg-carbonates, Ca- and Mg-sulfates, which can be mixed in reasonable proportions to replicate the chemical composition of the dust [2].

Intermediate albedo surfaces are widespread on Mars, and perhaps most prominent on Lunae Planum and Oxia in the circum-Chryse plateaus. The intermediate albedo unit is not a mixture of dust (bright) and basalt (dark), but a distinct unit with characteristic geologic and spectral properties. In Viking color, intermediate units appear "brown" to dark red, and are distinct in Phobos 2 ISM spectra: they are rich in water, contain little pyroxene, and contain more crystalline hematite than either bright or dark surfaces. The thermal inertias of intermediate albedo surfaces suggest fine-grained materials cemented together. Geologically, intermediate units appear as plateaus and wrinkle-ridged surfaces, swept clear of dust and basaltic sand. Channels and chasms cut through some intermediate surfaces appear to expose a laterally extensive layer, ~500 m thick, of cemented soils. In the circum-Chryse region, this layer is exposed from Noctis Labyrinthus to the edge of Oxia, approximately 5000 km east-west and 1000 km north-south [3].

The mineralogy of the intermediate albedo surfaces is poorly known. Lunae Planum is interpreted as flood basalt province, but

ISM spectra of the area show little pyroxene. The ISM spectra are consistent with hematite and a hydrous phase as the cements, and exposures of the cemented soils include both dark- and light-colored horizons. Another cementing phase, such as a hydrous iron oxide or sulfate, is possible. The dust clods at the VL sites were apparently cemented by a magnesium sulfate, but this may not be relevant to the intermediate surfaces [3].

The martian meteorites may provide important clues to the nature of cemented (intermediate albedo) surfaces on Mars. Almost all the martian meteorites contain secondary or alteration materials that were produced on Mars (conclusively preterrestrial in origin). These alteration materials come in three distinct assemblages. First, the shergottite meteorites contain very small quantities of a Ca-Mg salt assemblage, rich in Ca- and Mg-carbonates and sulfates. Also present are an Mg-phosphate, an aluminous (illitic) clay, and a poorly crystalline aluminosilicate containing significant S and Cl. The nakhlite meteorites all contain relatively abundant alteration materials (1–2 vol%) dominated by ferroan, low-Al smectite clays, which are rich in S, Cl, and P. Grains of ferrihydrite, hematite, Ca-sulfate, and Ca-Fe-Mn carbonates are also present. Finally, the ALH 84001 meteorite contains a Mg-Fe carbonate assemblage. It is dominated by ellipsoids of anhydrous carbonate minerals, which are zoned from Ca-rich cores to Mg-Fe mantles to pure Mg rims. Other minerals present include pyrite, magnetite, sphalerite, and a poorly defined iron sulfate. Of these alteration types, the clay-iron-mineral assemblage in the nakhlites is closest to the iron mineralogy implied by reflection spectra, although there is no spectroscopic evidence for clays on Mars. However, the assemblage in Nakhla is hydrothermal in origin, and thus a poor analog for widespread surface cementation. The Ca-Mg salt assemblage resembles the salt assemblage implied by reflection spectra in that it contains sulfate and carbonate minerals. Texturally, some of the carbonate minerals could originally have been hydrous. At this point, however, none of the alteration assemblages is a convincing match for the assemblages observed spectroscopically [2,4].

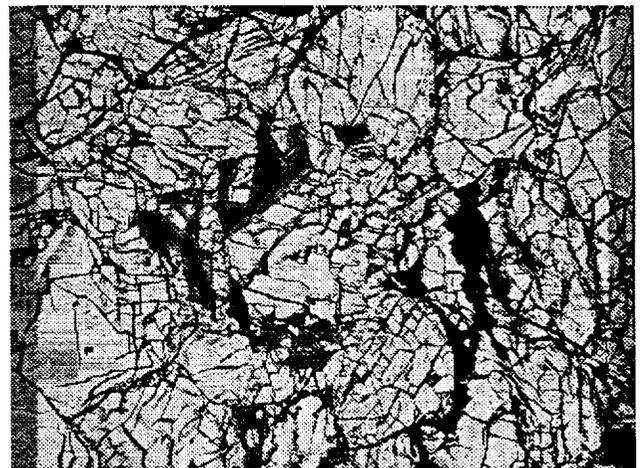


Fig. 1.

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From a sample return perspective, surface materials are among the easiest and most certain of collection. A sample of dust should be collected, at least as a contingency sample. The physical characteristics of the dust are crucial inputs to models of Mars' current climate; measuring these properties directly would greatly refine the models. If the dust represents the products of global erosion, its chemical composition and mineralogy will be critical to understanding the composition of Mars' crust (perhaps comparable to shales on Earth) and early planetary differentiation. If the dust represents singular volcanic events, its mineralogy and composition will define those events. Because dust is highly mobile in the present climate, it seems unlikely that drill cores through dust deposits will yield anything beyond more dust and cemented dust. Samples of cemented surfaces will provide direct evidence of the action of solvents, most likely water, in redistributing salts in the regolith. This evidence will be critical in unraveling Mars' ancient climate, and the mobility and stability of water at and near its surface.

References: [1] Clark B. et al. (1982) *JGR*, 87, 10059. Clark R. et al. (1990) *JGR*, 95, 14463. Murchie S. et al. (1993) *Icarus*, 105, 454. Bell J. III (1992) *Icarus*, 100, 575. Bell J. III et al. (1994) *Icarus*, 111, 106. Calvin W. et al. (1994) *JGR*, 99, 14659. Burns R. (1984) *LPS XXV*, 203. Blaney D. and McCord T. (1995) *JGR*, 100, 14433. Bell J. III et al. (1995) *JGR*, 100, 5297. Bishop J. and Pieters C. (1995) *JGR*, 100, 5369. Bishop J. et al. (1995) *Icarus*, 117, 101. Roush T. (1996) *JGR*, 101, 2215. Bell J. III (in press) in *Martian Spectroscopy*. [2] Gooding J. (1992) *Icarus*, 99, 28. [3] Clark B. and van Hart D. (1981) *Icarus* 45, 370. Presley M. and Arvidson R. (1988) *Icarus*, 75, 499. Christensen P. and Moore H. (1992) in *Mars*, 1135. Treiman A. et al. (1995) *JGR*, 100, 26339. Treiman A. (1996) *JGR*, 101, submitted. [4] Treiman A. et al. (1993) *Meteoritics*, 28, 86. Mittlefehldt D. (1994) *Meteoritics*, 29, 214. Treiman A. (1995) *Meteoritics*, 30, 294.

Viewgraphs presented at meeting—

Surface Materials on Mars

Three types of surface units

Dark

- ❖ Basaltic sand
- ❖ Basaltic bedrock

Bright

- ❖ Dust

Intermediate

- ❖ Duricrust or hardpan

Mineralogy of Dust—Viking

Titanomagnetite?

Fe-Ti in XRF analyses

Magnetic properties expt.

“Palagonite” (biology expt.)

Smectite clays

Nanophase Fe oxides

Adsorbed ozone/peroxide

Mg-sulfate cement

Mg-S in XRF analyses

Sample Collection

Dust is ubiquitous

From VL and orbital data, dust should be available at every site. (Mars' youngest basalt flows are under tens of centimeters dust!)

Hardpan surfaces extensive and possibly globe-circling

Can be mistaken for flood basalt

Could yield only samples of indurated dust

Mineralogy of Dust—Spectra

Ferric iron minerals

Nanophase hematite (e.g., Tharsis)

Ferrihydrite or Fe-doped clay (e.g., Arabia)

Additional mineral (?), a sulfate?

Sulfate

Scapolite??

Iron sulfate or sulfate-bearing Fe clay

Hydrous Mg-carbonate

Intermediate Albedo Surface—Duricrust or Hardpan

Stable surfaces clean of dust, sand

Oxia Palus

Lunae Planum

Cliffs exposed in Valles Marineris area

Consistent bright-dark layering from W. Noctis Labyrinthus beyond Ares Valles

Layering continuous beneath surface age boundary

Layering continuous beneath Noachian crater

Intermediate Albedo Spectra

≠ Dust + basalt!

Viking color—"brown"—dark red

PHOBOS ISM—"anomalous"

Much water

Little pyroxene

Crystalline hematite

Additional ferric phase (?) (sulfate?)

Cementing mineral?

Hydrous phase, not with iron??

Hematite

Ferric sulfate/ferric sulfate clay(?)

Martian Meteorite Alterations I

Ca-Mg salts (not abundant, shergottites)

Ca, Mg carbonates

Ca, Mg sulfates

Mg phosphate

Aluminous clay

S, Cl-bearing aluminosilicate

Martian Meteorite Alterations II

Fe-smectite (abundant, nakhlites)

Ferroan saponite clay

Ferrihydrite

Ca, (Fe, Mn) carbonates

Ca, Mg sulfates

Mg-Fe carbonate (abundant, ALH 84001)

Mg, Fe, Ca carbonates

Magnetite

Fe-sulfate (?)

Meteorite Clues to Surfaces

Dust—maybe

Composition can be modeled as mixture of igneous minerals, clays, salts from martian meteorite alterations

But composition also can be modeled as basalt

Duricrusts—maybe not

Ca-Mg salts (shergottites): Little iron, but maybe hydrous carbonates

Fe-smectite (nakhlites): Iron minerals, but T too high, ~70°C

Mg-Fe carbonate (ALH 84001): Not right iron minerals (magnetite, siderite), T uncertain

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Harry Y. McSween, University of Tennessee—

A Conservative Strategy for Geologic Sampling and Resource Utilization on Mars

A Mars sample return mission in 2005 will be a challenging task, one so ambitious that realistic goals must be made clear at the outset of planning. To help define what is realistic, I will focus on several "nuts-and-bolts" questions.

What kind of geologic sample(s) should (can) we collect, and why?

Both Viking lander sites had concentrations of rocks, possibly ejecta from local craters plus outcrops of layered rock. Small rock fragments were inferred to be scarce, but the rocks themselves showed considerable petrologic variability. The surface sampler was unable to chip or scratch any rock surfaces, implying no weak weathering rinds. Thermal inertia and albedo measurements for Mars are inversely correlated, suggesting mixtures of two materials: bright, low-inertia dust and dark, high-inertia rocks. Modeling of thermal inertia data indicates that surface rock cover averages 6%, with abundances ranging up to 35%. Both Viking lander sites have above average rock abundances (10% and 20%). Although periodically dusted with weathered material, the dark regions consistently reappear after dust activity, so exposures of bedrock are possible.

The mineralogy of the most easily accessible rocks is likely to resemble basaltic shergottites, based on spectral similarity of the dark, rocky regions (obtained by telescope and orbiting spacecraft) with these meteorites. The mineralogy of soils is unlikely to be represented by the alteration phases in SNC meteorites.

Advantages of collecting a soil sample are that it is ubiquitous and relatively easy to sample and provides information on interaction with the atmosphere and hydrosphere. If such a sample proves to be relatively unweathered, it may provide a great deal of petrologic diversity, analogous to lunar soil. However, it is likely that weathering would obscure such information. Rock samples allow the full arsenal of mineralogy/petrology/geochemistry/isotope techniques to be applied. The evidence in rocks is of discrete events rather than time-integrated events, as in soils. Both rocks and soil access the geologic past better than an atmospheric sample, and linkage with possible life will be more direct than with an atmospheric sample.

What information and tools are necessary for proper geologic sampling?

Instruments already scheduled to be flown on precursor missions are, for the most part, adequate to define a suitable site. On the sample collection mission itself, the following will be needed: descent imaging for geologic context, improved landing accuracy (probably more important for subsequent sample return missions), and mobility in the form of a reasonably capable rover. Mobility is especially critical because of the requirement (see below) to collect small rock samples, as well as to sample the petrologic diversity that is likely to have been provided by meteor impacts. It is not necessary to obtain a core sample on this first mission. Considerable attention

must be given to the possible need to sample large rocks. It is unlikely that rocks can be broken, but they might be drilled. However, mass, power, and cost limitations will probably require that the 2005 mission collect small rocks rather than sample larger ones.

A suggested sample payload is five small rocks (on the order of 10 g each), one loose soil sample, one duracrust sample, and possibly one atmospheric sample. This total sample size is roughly an order of magnitude smaller than that advocated at the last Mars sample return workshop (see *LPI Technical Report 88-07*). Sample storage can be very simple, e.g., soil can be used as packing for rocks, and atmosphere can be trapped as pore space or head space volume.

Sample storage requirements during launch, cruise, and reentry have already been specified by *NASA Technical Memorandum 4184*. This document includes recommendations on contamination, temperature, head-space pressure, radiation shielding, magnetism, and acceleration. As desirable as these target conditions are for maximizing the scientific worth of the samples, they may have to be relaxed for this mission to be flown under the cost constraints.

How can a returned sample help us find and utilize resources, or alternatively, what resources might be used to effect a sample return mission?

For the purposes of the 2005 mission, the only relevant martian resources are water and atmospheric carbon dioxide. An important goal of the Mars Surveyor Program is to understand the global inventory, long- and short-term repositories, and hydrologic cycle of water. This resource will certainly be critical for human exploration. However, water as a resource will probably not be directly addressed on this mission. Hydrous alteration phases in soil and rock may lead to a better understanding of one repository, but the energy required to extract water from hydrated minerals is considerably greater than from ice. Subsequent missions must address the question of where accessible water can be found. Although water is an economic propellant source, electrolysis to make H_2 and O_2 requires storing a hard cryogen.

The most accessible martian resource is atmospheric CO_2 , which can be obtained by simple compression with no mining or beneficiation required. When used for propellant production on Mars, it can significantly lower launch mass by eliminating fuel for the return trip plus the fuel required to boost the return fuel to Mars. Consideration should be given to *in situ* propellant production as a means of increasing the mass of the returned sample. The addition of *in situ* resource utilization would also make the mission more technologically exciting.

References: [1] *Workshop on Mars Sample Return Science* (1988) LPI Technical Report 88-07; *Scientific Guidelines for Preservation of Samples Collected from Mars* (1990) NASA Technical Memorandum 4184.

Viewgraphs presented at meeting—

Distribution of Rock and Soil

Lessons from Viking landers

Both sites have concentrations of rocks, possibly ejecta from local craters plus outcrops of layered rock

Small rock fragments are inferred to be scarce, and most centimeter-sized objects are interpreted as clods

Some rocks are dense and fine-grained, some may be breccias, and others appear to be vesicular

Surface sampler was unable to chip or scratch any rock surfaces, implying no weak rinds

Relevant remote sensing observations

Thermal inertia and albedo are inversely correlated, implying mixtures of two materials: bright, low-inertia dust and dark, high-inertia rocks

Modeling of thermal inertia data indicates that surface rock cover averages 6%, with abundances ranging up to 35%

Both Viking lander sites have above average rock abundances (10% and 20%), and VL2 is one of the rockiest regions on the planet

Although periodically dusted with weathered material, the dark regions consistently reappear after dust activity, so exposures of bedrock are possible

Advantages of Rocks vs. Soils

Soil advantages

Ubiquitous and relatively easy to sample

Lunar analogy—may provide petrologic diversity if unweathered

Gives information on interactions with the atmosphere and hydrosphere

Soil disadvantages

Eolian processes may limit diversity, and weathering may obscure desired information

Potential for revealing critical information about life is remote

Information in soils is cumulative (time-integrated)

Rock advantages

Can apply the full arsenal of petrology/geochemistry/isotope techniques

Igneous rocks give information on interior, stratigraphic chronology

Sedimentary rocks may give information on volatile inventories, past climates, life

Evidence is of discrete events rather than cumulative, as in soils

Rock disadvantages

Sampling unweathered rock may be challenging

Petrologic diversity may be limited by mass

Advantages of Either over Atmospheric Sample

Rocks and soil access the geologic past (rocks do this much better than soil)

Processes and chronology can be retrieved from rocks and possibly soils (through soil profiles)

Atmosphere can be analyzed remotely much better than rock or soil

Any linkage with life, if there was any, will be more direct with geologic samples

Measurements Required to Select Site and Samples

Mineralogy and chemistry

TES and GRS should provide global surveys

APX, EGA, spectra from lander should provide ground truth, identification of minerals in low abundance, modal information

Possible preliminary observations during sampling to select specific samples

High-resolution (probably descent) imaging

Integration with mineralogical and chemical data to determine petrology

Identify promising sample sites

Provide geologic context for the sampling site

Geophysical and geologic measurements

Moment of inertia and magnetic field constraints on planetary differentiation

Crater counting of target stratigraphic units

Regional geology of target sites to focus sampling

Getting to the right location

Landing accuracy

Improvements needed in reducing the landing ellipse (can be offset by mobility)

Mobility

Attempts to collect and analyze rocks failed at Viking lander sites, largely because of lack of mobility

Highland sites are likely to be heterogeneous

Sites of biologic or climatologic interest (lake beds, hydrothermal area) require mobility because of small size and complexity

Moving beyond the field of view adds excitement and scientific value, and allows sampling of geologic variety

Balloons are not suitable for sample return, because they cannot be directed to a specific location

Rovers with mature technology are too large for current program, and microrovers have limited distance and carrying capacity

Desired rover requirements: ability to move >5 km with a 5–10-kg payload

—(*Ames Workshop on Mobility, 1995*)

Sampling Devices

Obviously depends on soil vs. rock sample

Depends on sample numbers and masses (1–5 g rock, 0.5 g dust; see LPI Technical Report 88-07)

Need information on weathering rinds on rocks, consolidation of sediments

Representative rock sampling, diversity, and freshness require examination at handlens scale

Is it important to be able to break rocks?

Meaningful soil analyses require vertical profiles, e.g. coring

Decision should be made far in advance on type(s) of sample, so that development can be focused on robotic arms versus coring devices

Sample Storage Requirements During Launch, Cruise, and Reentry

Minimize contamination (1% elemental level)

Maintain at low temperature (<260 K for rock, <230 K for soil)

Maintain at low head-space pressure (<1 atm for rock, <0.01 atm for soil)

Shield ionizing radiation to 5 g/cm², monitor

Maintain magnetic field at < terrestrial

Keep acceleration to <7 g

—(*NASA Technical Memorandum 4184, 1990*)

Water

"Water is the resource"

—(*Mars Exploration Road Map, 1995*)

Global inventory

Geologic estimate (>440 m) extrapolated from erosion performed by floods

Geochemical estimates (<200 m) from atmospheric noble gases and SNC meteorites

Long- and short-term repositories

Polar deposits contain perhaps 20 m

Ground ice or water inferred from terrain softening at high latitudes, fluidized ejecta blankets

Storage capacity of the crust may be 1000 m

Hydrated minerals in regolith or hydrothermal deposits

Hydrologic cycle

Stable isotope fractionations in SNC meteorites suggest equilibrium exchange between atmosphere and hydrosphere, but not lithosphere

Modeling suggests a global cycle involving subpermafrost groundwater, polar ice, and atmosphere

Obtaining martian water

Need global mapping of near-surface water distribution

Need information on depth from penetrators or electrical resistivity measurements

Energy required to extract water from ice is considerably less than for hydrated minerals

While critical for exobiology, water is probably not an economic propellant source (electrolysis to make H₂ and O₂ requires storing a hard cryogen)

Atmospheric Carbon Dioxide

The most accessible martian resource

Atmosphere is 95% CO₂, available everywhere

Obtained by simple compression, with no mining or beneficiation required

Resource utility and justification

Used for propellant production on Mars

Significantly lowers launch mass by eliminating fuel for return trip plus fuel required to boost the return fuel to Mars

Fuels from ISRU technology

CH₄/O₂: CO₂ + 4H₂ = CH₄ + 2H₂O (required hydrogen is only 5% of the mass of fuel produced)

The production of other fuels and/or oxidants (e.g., hydrazines, alcohols, nitrogen tetroxide) is possible; there are tradeoffs between fuel performance and difficulty in handling and storage

OMIT TO
 ENI

Mike Drake, University of Arizona—

Mars Sample Return Program

These recommendations are based on discussion with an integration team consisting of Geoff Briggs, Chris McKay, Carolyn Porco, and Heinrich Wänke.

Focus: Did life ever get started on Mars?

Is it still there?

What geological and climatological conditions led to its formation and sustenance, or the lack thereof?

To accomplish that goal, we need a program of missions to:

Search for chemical, isotopic, physical indicators of life

Characterize martian geological environment through time

Characterize martian climatological environment through time

Evaluate resources for current robotic, future human exploration

Generally Agreed Upon Rules

Do not design a program that would generate the perception of failure early or ever —both finding and not finding life must be success indicators

Phased approach with measurable goals toward “the prize” with each mission

Inclusive strategy—most (all?) planetary science disciplines have contributions to make

Generally Agreed Upon First Mission Characteristics

Homogeneous site of larger area than landing ellipse

Three broad classes of landing site

- ❖ volcanic terrains
- ❖ ancient brecciated highlands
- ❖ ancient lake beds

Simple sample identification

Simple sample acquisition

Currently planned orbital and lander missions will provide adequate data for site selection

2001 (and 2003?) lander to first sample return site

Do not now need to establish exact site or sample return mission sequence

First Mission

Demonstrate end-to-end sample return capability

Look for evidence of past life as part of planetary protection studies

Prove or disprove SNC/Mars connection

Lake-Bed Mission Opportunity

Lander with rover

Collect sample of atmosphere, loose soil, duricrust, one or more sediments

Either return samples or beacon beckons next mission

Accomplishments (not exclusive)

- ❖ Characterize sediment mineralogy, petrology, geochemistry, formation process
- ❖ Get age (?) of well-characterized surface—tie down crater-based chronology
- ❖ Search for past life—stable isotopes, physical fossils
- ❖ Calibrate “ground truth” for orbiting, *in situ* instruments

Dangers (not exclusive)

- ❖ High elevation site could be tricky
- ❖ We don't know there are coherent lake sediments
- ❖ We don't know that we can sample sediments

Volcanic Area Mission Opportunity

Lander with rover

Collect sample of atmosphere, loose soil, duricrust, one-or-more hard rocks

Either return sample or beacon beckons next mission

Accomplishments (not exclusive)

- ❖ Search duricrust for stable isotope evidence of past life
- ❖ Search for past magnetic field (imp. for life)
- ❖ Characterize hard rock mineralogy, petrology, geochemistry, formation process
- ❖ Get age of well-characterized surface - tie down crater-based chronology
- ❖ Calibrate “ground truth” for orbiting, *in situ* instruments

Dangers (not exclusive)

- ❖ Goldin, Congress, public might get bored if we find a SNC but no life

Ancient Highland Breccia Mission Opportunity

Lander with rover

Collect sample of atmosphere, loose soil, duricrust, one-or-more breccias and other rocks

Either return samples or beacon beckons next mission

Accomplishments (not exclusive)

- ❖ Characterize highland igneous, mineralogy, petrology, geochemistry, breccia formation process
- ❖ Get age (?) of well-characterized surface—tie down crater-based chronology
- ❖ Search for past life (?)—hydrothermal alteration?
- ❖ Calibrate “ground truth” for orbiting, *in situ* instruments
- ❖ Get sample of ancient as well as modern atmosphere

Dangers (not exclusive)

- ❖ High elevation site could be tricky
- ❖ We don't know there are coherent breccias
- ❖ We don't know that we can sample breccias

Subsequent Opportunities

TBD

- ❖ Hot spring deposits
- ❖ Hydrothermally altered areas
- ❖ ???????????

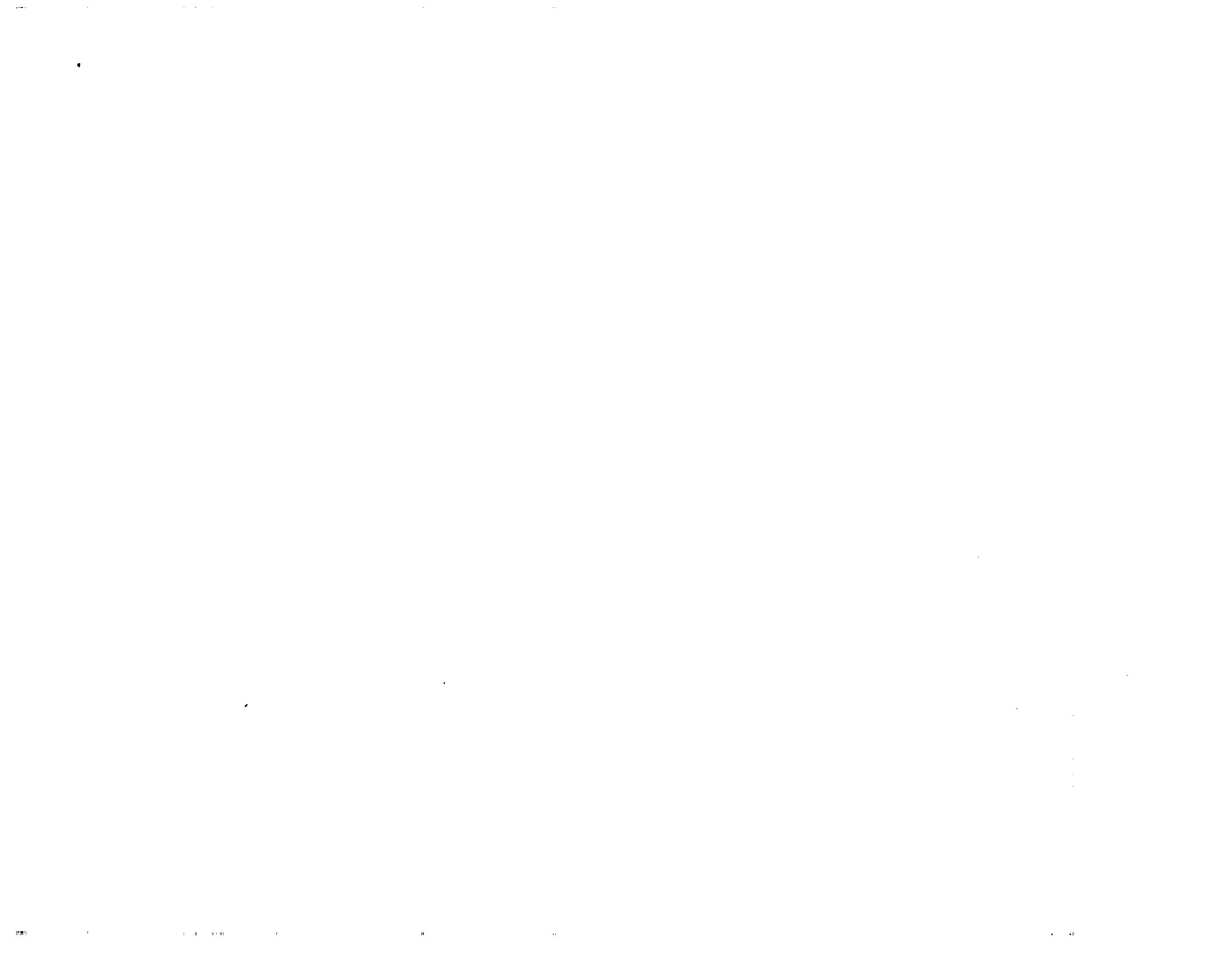
Issues Needing Thought

Sample Return in 2003?

- ❖ INTERMARSNET?
- ❖ Too expensive?
- ❖ Too fast?
- ❖ Collect in 2003, return in 2005?
- ❖ Reconnaissance in 2003, collect samples in 2005?

Recommendation

- ❖ Science and Implementation (McCleese) Committee to study the following for each proposed class of landing site
 - ◆ Sample identification
 - ◆ Sample selection—which samples to bring back—masses
 - ◆ Sample acquisition
 - ◆ Sample container sealing
 - ◆ Trade of large volume/mass atmosphere sample for more solid matter
 - ◆ Sample return cruise environment
 - ◆ Sample curation
 - ◆ JSC?
 - ◆ CDC?
 - ◆ Development and purchase of laboratory instruments



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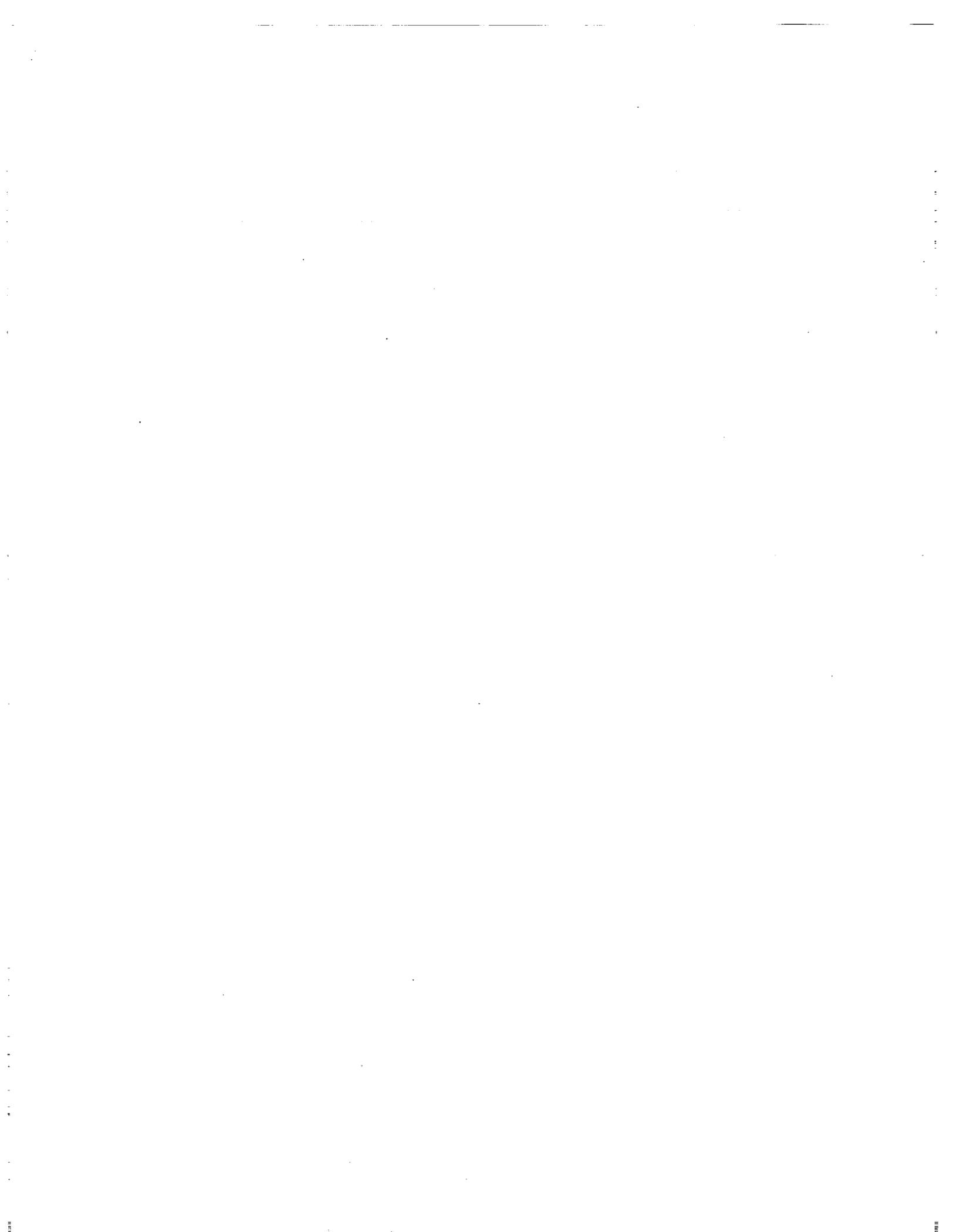
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